

ARSENIC

CONTINUING EDUCATION
PROFESSIONAL DEVELOPMENT COURSE



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State Approval Listing URL...

<http://www.tlch2o.com/PDF/CEU%20State%20Approvals.pdf>

You can obtain a printed version from TLC for an additional \$49.95 plus shipping charges.

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News of Science, Medicine, and Technology

The Arsenic Eliminator

by Fenella Saunders

When the Bush administration declined to tighten standards for arsenic in drinking water, its argument focused on economics: Limiting the heavy metal to 10 parts per billion, as the World Health Organization recommends, would cost too much. Xiaoguang Meng begs to differ.

He and colleague George Korfiatis, both at Stevens Institute of Technology in New Jersey, have developed a filtration system cheap enough for villagers in Bangladesh, where groundwater is naturally contaminated with arsenic. Meng's process requires just two buckets, some sand, and a tea-bag-sized packet of iron-based powder. Pour tainted water into one bucket, along with the powder, and stir.

Arsenic bonds to the iron and coagulates out of the water. After a minute, pour the mix into a second bucket filled with 4 inches of sand.



Photo by Kathy Cacicedo.

The sand filters out the arsenic-iron particles, leaving the water pure. In yearlong pilot tests with 300 Bangladeshi families, Meng measured arsenic concentrations in well water as high as 648 parts per billion. The bucket filter reduced that to 10 parts per billion, at a cost of about \$2 a year per family.

Even 50 parts per billion, the legal limit in the United States, may carry a 1-in-100 lifetime risk of cancer, according to a recent National Academy of Sciences study. Some American water treatment plants are moving beyond federal rules and testing a scaled-up version of the Stevens decontamination system.

"European countries already use the WHO standard, so why can't we? It doesn't make sense," Meng says.

Purpose of this Document

This document provides guidance to States, Tribes, and U.S. Environmental Protection Agency (EPA) Regions exercising primary enforcement responsibility under the Safe Drinking Water Act (SDWA).

Throughout this document, the terms “State” or “States” are used to refer to all types of primacy agencies including U.S. territories, Indian tribes, and EPA regions. The SDWA provisions and EPA regulations described in this document contain legally binding requirements. This document does not substitute for those provisions or regulations, nor is it a regulation itself.

Thus, it does not impose legally binding requirements on the EPA, States, Tribes, or the regulated community, and may not apply to a particular situation based upon the circumstances. The EPA, State, and Tribal decision makers retain the discretion to adopt approaches on a case-by-case basis that differ from this guidance where appropriate. Any decisions regarding a particular facility will be made based on the applicable statutes and regulations.

Therefore, interested parties are free to raise questions and objections about the appropriateness of the application of this guidance to a particular situation, and the EPA will consider whether or not the recommendations or interpretations in the guidance are appropriate in that situation. The EPA may change this guidance in the future.

This course is intended to be used as a screening tool for arsenic treatment technologies. It provides descriptions of the theory, design, and operation of the technologies; information on commercial availability and use; performance and cost data, where available; and a discussion of factors affecting effectiveness and cost.

As a technology overview document, the information can serve as a starting point for identifying options for arsenic treatment. The feasibility of particular technologies will depend heavily on site-specific factors, and final treatment and remedy decisions will require further analysis, expertise, and possibly treatability studies.

Most of the information sources used for this report contain information about treatments of environmental media and drinking water. Only limited information was identified about the treatment of industrial waste and wastewater containing arsenic.

This does not necessarily indicate that treatment of industrial wastes and wastewater containing arsenic occurs less frequently, because data on industrial treatments may be published less frequently.

The authors and reviewers of this course identified these information sources based on their experience with arsenic treatment.

Important Information about this Manual

Disclaimer

This manual has been prepared to assist employees in the general awareness of the Arsenic treatment and remediation process including: water distribution systems and groundwater production systems, complex pumping ideas, dangerous excavation techniques, water regulatory sampling and dealing with often-complex procedures and requirements for safely handling hazardous and toxic materials. The scope of the material is quite large, requiring a major effort to bring it under control. Employee health and safety, as well as that of the public, depend upon careful application of federal and state regulations and safe working procedures.

This manual will cover general laws, regulations, required procedures and work rules relating to water distribution and sampling. It should be noted, however, that the federal and state regulations are an ongoing process and subject to change over time. For this reason, a list of resources and hyperlinks is provided to assist in obtaining the most up-to-date information on various subjects. You can find these on our website or in this manual.

This manual is a guidance document for employees who are involved with Arsenic treatment, handling, water quality and pollution control. It is not designed to meet the full requirements of the United States Environmental Protection Agency (**EPA**) or the Department of Labor-Occupational Safety and Health Administration (**OSHA**) rules and regulations.

This course manual will provide general guidance and should not be used as a preliminary basis for developing general water/wastewater sampling plans or water distribution safety plans or procedures. This document is not a detailed water/wastewater textbook or a comprehensive source book on water/wastewater/safety rules and regulations.

Technical Learning College makes no warranty, guarantee or representation as to the absolute correctness or appropriateness of the information in this manual and assumes no responsibility in connection with the implementation of this information.

It cannot be assumed that this manual contains all measures and concepts required for specific conditions or circumstances. This document should be used for guidance and is not considered a legal document.

Individuals who are responsible for water distribution, production and/or sampling and the health and safety of workers at hazardous waste sites should obtain and comply with the most recent federal, state, and local regulations relevant to these sites and are urged to consult with OSHA, the EPA and other appropriate federal, state and local agencies.

Course Description

Arsenic CEU Training Course

The purpose of this CEU course is to provide a synopsis of the availability, performance, and cost of 13 various arsenic treatment technologies for soil, water, and wastewater. Its intended audience includes hazardous waste site managers; generators and treaters of arsenic-contaminated waste and wastewater; owners and operators of drinking water/wastewater treatment plants; regulators; and industrial waste/pretreatment inspectors.

General Course Objective

This course will review the EPA Arsenic Rule and different Arsenic removal devices and methods. This course will cover water and wastewater fundamentals/principles along with basic chemistry. This course is general in nature and not state specific. You will not need any other materials for this course.

Audience

Attention Pretreatment Operators, Laboratory Technicians, Water Distribution, Well Drillers, Pump Installers, and Water and Wastewater Treatment Operators. The target audience for this course is the person interested in working in a water treatment or distribution facility and wishing to maintain CEUs for certification license, meet education needs for promotion, or to learn how to do the job more safely and effectively.

Statement of Need

It is essential that all water and wastewater operators learn to deal with Arsenic. Arsenic is a priority pollutant being a threat to the wastewater treatment system. Water systems need to monitor for Arsenic to verify that the water they provide to the public meets all federal and state standards. Currently, the nation's community water systems (CWSs) and nontransient non-community water systems (NTNCWSs) must monitor for more than 83 contaminants including Arsenic. This course will focus on the metalloids and related inorganic chemical (elemental) contaminants. You will learn the EPA rule concerning Arsenic and proper sampling techniques and various Arsenic treatment methods.

Inorganic Compounds (IOCs)

Inorganic compounds are rather simple chemicals present in ground water. These chemicals are generally described as mineral in nature and usually exist as ions (chemical substances with a positive or negative charge) when dissolved in water. Typical examples include sodium, iron, calcium, magnesium, manganese, nitrate, chloride, sulfate, and zinc. Many of these chemicals are naturally occurring minerals that are dissolved from the rock/soil which make up the aquifer or water-bearing rock formations below the soil surface. However, some of these compounds may be introduced into ground water by human activities. Nitrate (an agricultural fertilizer) and sodium chloride (road salt) are two examples. Water purveyors need to test for 30 different inorganic compounds including all arsenic, barium, cadmium, lead, mercury, selenium, and thallium

Metalloid Section

Arsenic, boron, silicon, germanium, antimony and tellurium are commonly classified as metalloids. One or more from among selenium, polonium or astatine are sometimes added to the list. Boron is sometimes excluded from the list, by itself or together with silicon. Tellurium is sometimes not regarded as a metalloid. The inclusion of antimony, polonium and astatine as metalloids has also been questioned. A metalloid is a chemical element with properties that are in-between or a mixture of those of metals and nonmetals, and which is considered to be difficult to classify unambiguously as either a metal or a nonmetal.

Prerequisites: None

Final Examination for Credit

Opportunity to pass the final comprehensive examination is limited to three attempts per course enrollment.

Course Procedures for Registration and Support

All of Technical Learning College's (TLC) correspondence courses have complete registration and support services offered. Delivery of services will include, e-mail, web site, telephone, fax and mail support. TLC will attempt immediate and prompt service. When students register for a distance or correspondence course, they'll be assigned a start date and an ending date.

It is the student's responsibility to note dates for assignments and keep up with the course work. If a student falls behind, he/she must contact TLC and request an ending date extension in order to complete the course. It is the prerogative of TLC to decide whether to grant the request. All students will be tracked by their social security number or a unique number.

Disclaimer and Security Notice

The student shall understand that it their responsibility to ensure that this CEU course is either approved or accepted in my State for CEU credit. The student shall understand and follow State laws and rules concerning distance learning courses and understand these rules change on a frequent basis and will not hold Technical Learning College responsible for any changes. The student shall understand that this type of study program deals with dangerous conditions and will not hold Technical Learning College, Technical Learning Consultants, Inc. (TLC) liable for any errors or omissions or advice contained in this CEU education training course or for any violation or injury caused by this CEU education training course material. The student shall contact TLC if they need help or assistance and double-check to ensure my registration page and assignment has been received and graded.

Student Verification

The student shall submit a driver's license for signature verification and track their time worked on the assignment. The student shall sign an affidavit verifying they have not cheated and worked alone on the assignment. All student attendance is tracked on the student attendance database.

Feedback Mechanism (examination procedures)

Each student will receive a feedback or survey form as part of his or her study packet. You will be able to find this form in the front of the assignment lesson. The student can e-mail, snail mail or telephone TLC for any concern at any time. Most of these concerns will be answered in 2 hours but not more than 24 hours. TLC has three support staff administrators with modern computers and all have excellent communication and computer skills able to respond and track all students and required forms and assignment. We have a dedicated computer student tracking system database that is backed-up on a daily based and this information is secured and stored at a secure offsite location.

TLC Contact Information

All instructors and administrative staff are obligated to respond within 1 day by email, snail mail or telephone providing proper guidance to successfully complete the assignment. Email and telephone inquiries are handled quickly, generally within 2 hours of the call. We encourage students to complete their work with less frustration and fewer delays by calling or e-mailing us for any concern. We attempt to provide direct interaction similar to conventional classroom training.

Security and Integrity

All students are required to do their own work. All lesson sheets and final exams are not returned to the student to discourage sharing of answers. Any fraud or deceit and the student will forfeit all fees and the appropriate agency will be notified. A random test generator will be implemented to protect the integrity of the assignment.

Student Information Personal Data Security Procedures

All information regarding the student is strict and privileged only. This information is held in secure databases and is not sold or provided to any one unless the student requests a copy or a State agency does an audit. Even during audits, we restrict confidential information unless the Agency can provide a legitimate excuse. Some of this security information and data is priority and details are not provided. Students are not provided with any passwords at this time.

Final Assignment

The final examination assignment is determined by the examination administrator or the instruction and there are generally three versions that are readily available. There is also three levels of the examination from average, (5 Answers) Difficult (5 +All of the above) and very difficult (Six answers and All of the above). The student is provided the average rated examination unless there is a condition or concern that requires a more difficult examination. Example, two or more students at the same address or any suspicion of cheating or potential fraud.

Failure

If the student fails the examination, they are provided with two more chances to successfully pass the exam with a score of 70% or better. The student may receive a different and randomly generated exam. Upon failure of an exam, the student can submit their concerns in writing or submit a survey form and has the option to receive instructor assistance that would be equivalent to conventional classroom assistance in discovering the areas that are deficient. The instructor has the option in describing the assistance method or procedure depending upon the student's deficiencies.

Forfeiture of Certificate (Cheating)

If a student is found to have cheated on an examination, the penalty may include--but is not limited to--expulsion; foreclosure from future classes for a specified period; forfeiture of certificate for course/courses enrolled in at TLC; or all of the above in accordance with TLC's Student Manual. A letter notifying the student's sponsoring organization (State Agency) of the individual's misconduct will be sent by the appropriate official at TLC. No refund will be given for paid courses. An investigation of all other students that have taken the same assignment within 60 day period of the discovery will be re-examined for fraud or cheating. TLC reserves the right to revoke any published certificates and/or grades if cheating has been discovered for any reason and at any time. Students shall sign affidavit agreeing with all security measures. The student shall submit a driver's license for signature verification and track their time worked on the assignment. The student shall sign an affidavit verifying they have not cheated and worked alone on the assignment.

Disclaimer and Security Notice

The student shall understand that it their responsibility to ensure that this CEU course is either approved or accepted in my State for CEU credit. The student shall understand and follow State laws and rules concerning distance learning courses and understand these rules change on a frequent basis and will not hold Technical Learning College responsible for any changes. The student shall understand that this type of study program deals with dangerous conditions and will not hold Technical Learning College, Technical Learning Consultants, Inc. (TLC) liable for any errors or omissions or advice contained in this CEU education training course or for any violation or injury caused by this CEU education training course material.

Student Assistance

The student shall contact TLC if they need help or assistance and double-check to ensure my registration page and assignment has been received and graded.

Instructions for Written Assignments

The Arsenic training CEU course uses multiple choice and true/false questions. Answers may be written in this manual or typed out on a separate answer sheet. TLC prefers that students type out and e-mail their answer sheets to info@tlch2o.com, but they may be faxed to (928) 468-0675.

Grading Criteria

TLC offers students the option of either pass/fail or assignment of a standard letter grade. If a standard letter grade is not requested, a pass/fail notice will be issued. Final course grades are based on the total number of possible points. The grading scale is administered equally to all students in the course. Do not expect to receive a grade higher than that merited by your total points. No point adjustments will be made for class participation or other subjective factors. For security purposes, please fax or e-mail a copy of your driver's license and always call us to confirm we've received your assignment and to confirm your identity.

Final Examination for Credit

Opportunity to pass the final comprehensive examination is limited to three attempts per course enrollment.

Required Texts

This course comes complete and does not require any other materials.

Feedback Mechanism (Examination Procedures)

A feedback form is included in the rear of each study packet.

Environmental Terms, Abbreviations, and Acronyms

TLC provides a glossary in the rear of this manual that defines, in non-technical language, commonly used environmental terms appearing in publications and materials, as well as abbreviations and acronyms used throughout the EPA and other governmental agencies.

Record Keeping and Reporting Practices

TLC keeps all student records for a minimum of five years. It is the student's responsibility to give the completion certificate to the appropriate agencies.

ADA Compliance

TLC will make reasonable accommodations for persons with documented disabilities. Students should notify TLC and their instructors of any special needs. Course content may vary from this outline to meet the needs of these particular students.

Proctoring Instructions

Students enrolled in Technical Learning College's CEU courses that require proctored testing and **who do not live in the physical service area** of the Technical Learning College Test Center must nominate and gain prior approval of a proctor who will monitor course tests. A new proctor nomination form is required for each term and for each class.

PROCTORS, If Necessary...

A proctor is an individual who agrees to receive and administer a student's test(s) from Technical Learning College at the proctor's business email address. The test(s) will be ethically and professionally administered in a suitable testing environment (e.g., college/library or professional office). The proctor will return the test(s) to the Technical Learning College Test Center via fax immediately after administration, and the proctor will mail the exam within one (1) work day of administration to the Technical Learning College Test Center.

Proctors certify in writing to the Technical Learning College Test Center that the student completed the test according to all of the specific directions provided in the proctor guidelines letter. As the Proctor Nomination Form indicates, the student will identify the specific test(s) the proctor will monitor.

Any proctor the student nominates must be acting in the official capacity in one of the following positions:

- **College or University Personnel:** Dean, Department Chair, Student Records, Professional Staff Member of an adult/continuing education office or counseling center, Librarian, Professor, or any official testing center personnel if the tests are administered in the center.
- **Armed Forces Education Office Personnel**

- **Public or Private School Personnel:** Superintendent, Principal, Guidance Counselor, or Librarian.
- **Other:** Civil Service Examiner, Librarian for City/County, HR Professional, or Education/Training Coordinator.

The following persons do not qualify as proctors:

- **Co-workers, someone who reports to you or your immediate supervisor**
- **Friends**
- **Neighbors**
- **Relatives**

NOMINATING A PROCTOR

Students are responsible for identifying, nominating, and making all of the arrangements for the proctoring of their course tests, including the payment of any fees for services and the return of test materials to Technical Learning College Test Center (cost of FAX or postage). The proctor must be able to receive the student's test(s) via email as attachments. The Technical Learning College Test Center does not accept Yahoo, AOL, G-mail, Hotmail, or etc. email addresses.

If the student is unable to find a suitable proctor, s/he must contact the Technical Learning College Test Center for assistance immediately via email.

PROCTOR NOMINATION FORM

Students will use the Proctor Nomination Form for nomination and approval of a proctor. The student will complete the top part of the form for each course s/he is taking, even if the same proctor is used for all tests. The student must click on the submit button for the data to be electronically transmitted to the Technical Learning College Test Center.

DISCLAIMER NOTICE

I understand that it is my responsibility to ensure that this CEU course is either approved or accepted in my State for CEU credit. I understand State laws and rules change on a frequent basis and I believe this course is currently accepted in my State for CEU or contact hour credit, if it is not, I will not hold Technical Learning College responsible. I also understand that this type of study program deals with dangerous conditions and that I will not hold Technical Learning College, Technical Learning Consultants, Inc. (TLC) liable for any errors or omissions or advice contained in this CEU education training course or for any violation or injury caused by this CEU education training course material. I will call or contact TLC if I need help or assistance and double-check to ensure my registration page and assignment has been received and graded.

AFFIDAVIT OF EXAM COMPLETION

I affirm that I personally completed the entire text of the course. I also affirm that I completed the exam without assistance from any outside source. I understand that it is my responsibility to file or maintain my certificate of completion as required by the state or by the designation organization.

Note to Students

Keep a copy of everything that you submit! If your work is lost, you can submit your copy for grading. If you do not receive your certificate of completion or other results within two to three weeks after submitting it, please contact your instructor.

When the Student finishes this course...

At the finish of this course, you (the student) should be able to explain and describe the various metalloids and inorganic contaminants found in water while focusing on properly identifying Arsenic and proper water treatment or filtration methods. You will learn proper Arsenic sampling methods and various treatment techniques. You will learn the various types of Arsenic and the dangers Arsenic presents to the public.

Educational Mission

The educational mission of TLC is:

To provide TLC students with comprehensive and ongoing training in the theory and skills needed for the environmental education field,

To provide TLC students opportunities to apply and understand the theory and skills needed for operator certification and environmental education,

To provide opportunities for TLC students to learn and practice environmental educational skills with members of the community for the purpose of sharing diverse perspectives and experience,

To provide a forum in which students can exchange experiences and ideas related to environmental education,

To provide a forum for the collection and dissemination of current information related to environmental education, and to maintain an environment that nurtures academic and personal growth.

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Arsenic Check



Arsenic enters groundwater from the erosion of arsenic containing rocks and soil.

Groundwater contaminated with arsenic has been found in 49 of the 50 states in the U.S. Recent debate over changing the U.S. limit as well as the problems in India and Bangladesh have made arsenic a hot topic.

This arsenic test kit provides a safe, reliable and simplified method to test for the presence of arsenic in water from 5 ppb to over 800 ppb. Inorganic arsenic compounds in the water sample are converted to arsine (AsH_3) gas by a reaction between zinc powder and a mild acid powder.

A test strip sensitive to the arsine gas is used to indicate the presence and concentration of arsenic in the water sample. A complete test requires about 30 minutes.

Two water samples can be tested simultaneously with the included test kit components.

- Tested by an independent laboratory to be accurate and reliable
- Non-hazardous reagents & easy to follow test procedure
- No Interference from H_2S up to 2ppm
- No Iron or Sulfate interference
- Test detects both As^{+3} and As^{+5}

Contact Lab Safety.

1-800-356-0783, www.labsafety.com

For our Arsenic test, reference the EPA website:

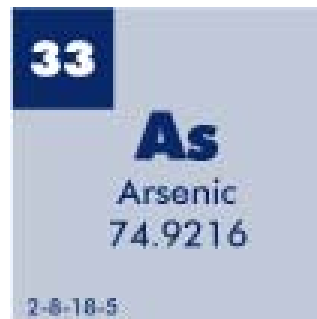
Verification report

http://www.epa.gov/etv/pdfs/vr/vs/01_vr_quick.pdf

Verification Statement

http://www.epa.gov/etv/pdfs/vr/vs/01_vs_quick.pdf

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Definitions Larger Glossary in the rear.

As used in 40 CFR 141, the term:

Best available technology (BAT) means the best technology, treatment techniques, or other means which the Administrator finds, after examination for efficacy under field conditions and not solely under laboratory conditions, are available (taking cost into consideration). For the purposes of setting MCLs for synthetic organic chemicals, any BAT must be at least as effective as granular activated carbon.

Community water system (CWS) means a public water system which serves at least 15 service connections used by year-round residents or regularly serves at least 25 year-round residents.

Compliance cycle means the nine-year calendar year cycle during which public water systems must monitor. Each compliance cycle consists of three three-year compliance periods.

Compliance period means a three-year calendar year period within a compliance cycle. Each compliance cycle has three three-year compliance periods.

Contaminant means any physical, chemical, biological, or radiological substance or matter in water.

Maximum contaminant level (MCL) means the maximum permissible level of a contaminant in water which is delivered to any user of a public water system.

Maximum contaminant level goal (MCLG) means the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety. Maximum contaminant level goals are nonenforceable health goals.

Non-transient non-community water system (NTNCWS) means a public water system that is not a community water system and that regularly serves at least 25 of the same persons over 6 months per year.

Point-of-entry treatment device (POE) is a treatment device applied to the drinking water entering a house or building for the purpose of reducing contaminants in the drinking water distributed throughout the house or building.

Point-of-use treatment device (POU) is a treatment device applied to a single tap used for the purpose of reducing contaminants in drinking water at that one tap.



Public water system (PWS) means a system for the provision to the public of water for human consumption through pipes or, after August 5, 1998, other constructed conveyances, if such system has at least fifteen service connections or regularly serves an average of at least twenty-five individuals daily at least 60 days out of the year. Such term includes: any collection, treatment, storage, and distribution facilities under control of the operator of such system and used primarily in connection with such system; and any collection or pretreatment storage facilities not under such control which are used primarily in connection with such system. Such term does not include any "*special irrigation district*."

A public water system is either a "community water system" or a "noncommunity water system."

State means the agency of the State or Tribal government which has jurisdiction over public water systems. During any period when a State or Tribal government does not have primary enforcement responsibility pursuant to section 1413 of the Act, the term "State" means the Regional Administrator, U.S. Environmental Protection Agency.

Surface water means all water which is open to the atmosphere and subject to surface runoff.



Ion Exchange Units

Ion exchange technology is one method to remove Arsenic from drinking water.

List of Acronyms and Abbreviation

AA Activated alumina	HTMR High temperature metals recovery
AC Activated carbon	MCL Maximum Contaminant Level (enforceable drinking water standard)
ASR Annual Status Report	MF Microfiltration
As(III) Trivalent arsenic, common inorganic form in water is arsenite, H_3AsO_3	MHO Metallurgie-Hoboken-Overpelt
As(V) Pentavalent arsenic, common inorganic form in water is arsenate, H_2AsO_4	mgd million gallons per day
BDAT best demonstrated available technology	mg/kg milligrams per kilogram
BTEX Benzene, toluene, ethylbenzene, and xylene	mg/L milligrams per Liter
CCA Chromated copper arsenate	NF Nanofiltration
CERCLA Comprehensive Environmental Response, Compensation, and Liability Act	NPL National Priorities List
CERCLIS 3 CERCLA Information System	OCLC Online Computer Library Center
CLU-IN EPA's CLeanUp INformation system	ORD EPA Office of Research and Development
CWS Community Water System	OU Operable Unit
cy Cubic yard	PAH Polycyclic aromatic hydrocarbons
DDT Dichloro-diphenyl-trichloroethane	PCB Polychlorinated biphenyls
DI Deionized	POTW Publicly owned treatment works
DOC Dissolved organic carbon	PRB Permeable reactive barrier
DoD Department of Defense	RCRA Resource Conservation and Recovery Act
DOE Department of Energy	Redox Reduction/oxidation
EDTA Ethylenediaminetetraacetic acid	RO Reverse osmosis
EPA U.S. Environmental Protection Agency	ROD Record of Decision
EPT Extraction Procedure Toxicity Test	SDWA Safe Drinking Water Act
FRTR Federal Remediation Technologies Roundtable	SMZ surfactant modified zeolite
ft feet	SNAP Superfund NPL Assessment Program
GJO DOE's Grand Junction Office	S/S Solidification/Stabilization
gpd gallons per day	SVOC Semivolatile organic compounds
gpm gallons per minute	TCLP Toxicity Characteristic Leaching Procedure
	TNT 2,3,6-trinitrotoluene
	TWA Total Waste Analysis
	UF Ultrafiltration
	VOC Volatile organic compounds
	WET Waste Extraction Test
	ZVI Zero valent iron

A PDF version of *Arsenic Treatment Technologies for Soil, Waste, and Water*, is available for viewing or downloading from the Hazardous Waste Cleanup Information (CLU-IN) system web site at <http://clu-in.org/arsenic>.

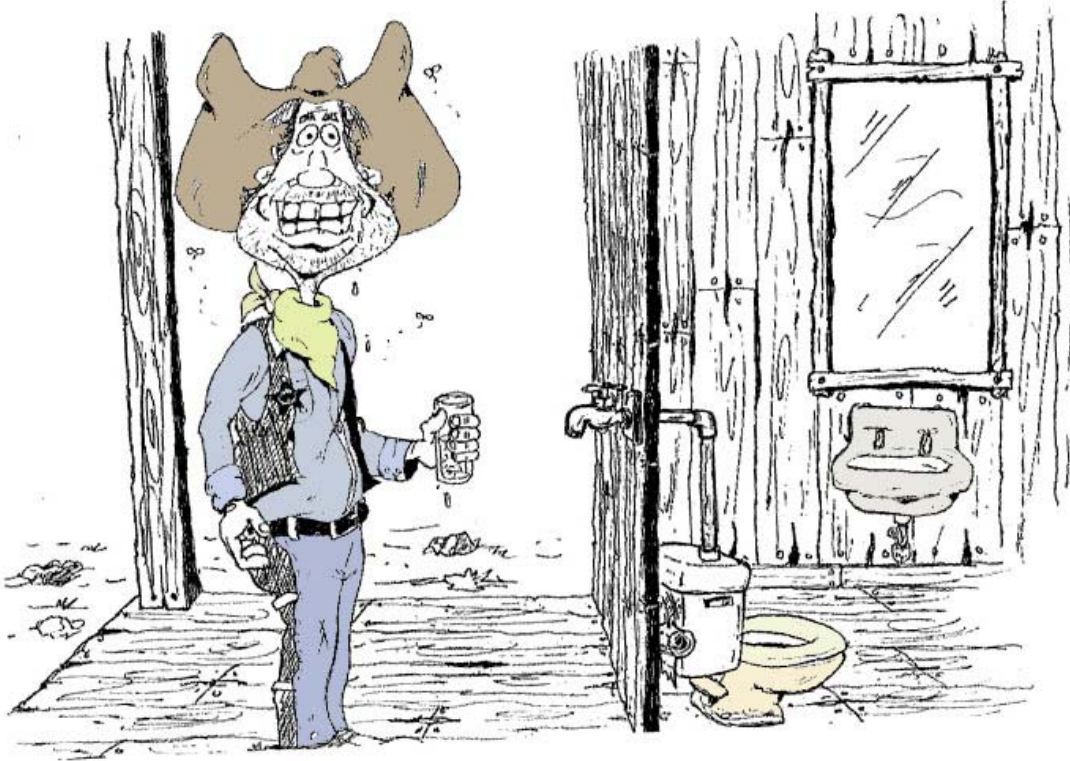
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KNOW YOUR "SOURCE" WATER!



WATERBORNE DISEASES: A disease, caused by a virus, bacterium, protozoan, or other microorganism, capable of being transmitted by water (e.g., typhoid fever, cholera, amoebic dysentery, gastroenteritis).

Arsenic Introduction

Arsenic- Inorganic Contaminant 0.010 mg/L MCL Metalloid

Arsenic is a chemical element with symbol **As** and the atomic number is 33. Arsenic occurs in many minerals, usually in conjunction with sulfur and metals, and also as a pure elemental crystal. It was first documented by Albertus Magnus in 1250. Arsenic is a metalloid. It can exist in various allotropes, although only the gray form has important use in industry.



In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG).

Contaminants are any physical, chemical, biological or radiological substances or matter in water.

The MCLG for arsenic is zero. EPA has set this level of protection based on the best available science to prevent potential health problems. Based on the MCLG, EPA has set an enforceable regulation for arsenic, called a maximum contaminant level (MCL), at 0.010 mg/L or 10 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies.

The Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring Final Rule, the regulation for arsenic, became effective in 2002. The Safe Drinking Water Act requires EPA to periodically review and revise contaminants, if appropriate, based on new scientific data. The regulation for arsenic will be included in a future review cycle.

The main uses of metallic arsenic is for strengthening alloys of copper and especially lead (for example, in car batteries). Arsenic is a common n-type dopant in semiconductor electronic devices, and the optoelectronic compound gallium arsenide is the most common semiconductor in use after doped silicon. Arsenic and its compounds, especially the trioxide, are used in the production of pesticides (treated wood products), herbicides, and insecticides. These applications are declining, however.

Arsenic is notoriously poisonous to multicellular life, although a few species of bacteria are able to use arsenic compounds as respiratory metabolites. Arsenic contamination of groundwater is a problem that affects millions of people across the world.

Arsenic, a naturally occurring element, is found throughout the environment; for most people, food is the major source of exposure. Acute (short-term) high-level inhalation exposure to arsenic dust or fumes has resulted in gastrointestinal effects (nausea, diarrhea, abdominal pain); central and peripheral nervous system disorders have occurred in workers acutely exposed to inorganic arsenic. Chronic (long-term) inhalation exposure to inorganic arsenic in humans is associated with irritation of the skin and mucous membranes. Chronic oral exposure has resulted in gastrointestinal effects, anemia, peripheral neuropathy, skin lesions, hyperpigmentation, and liver or kidney damage in humans. Inorganic arsenic exposure in humans, by the inhalation route, has been shown to be strongly associated with lung cancer, while ingestion of inorganic arsenic in humans has been linked to a form of skin cancer and also to bladder, liver, and lung cancer. EPA has classified inorganic arsenic as a Group A, human carcinogen.

Contamination of Groundwater

Arsenic contamination of groundwater is often due to naturally occurring high concentrations of arsenic in deeper levels of groundwater. It is a high-profile problem due to the use of deep tubewells for water supply in the Ganges Delta, causing serious arsenic poisoning to large numbers of people. In addition, mining techniques such as hydraulic fracturing mobilize arsenic in groundwater and aquifers due to enhanced methane transport and resulting changes in redox conditions, and inject fluid containing additional arsenic.

A 2007 study found that over 137 million people in more than 70 countries are probably affected by arsenic poisoning of drinking water. Arsenic contamination of ground water is found in many countries throughout the world, including the USA.

Approximately 20 incidents of groundwater arsenic contamination have been reported from all over the world. Of these, four major incidents were in Asia, including locations in Thailand, Taiwan, and Mainland China. In South America, Argentina and Chile are affected. There are also many locations in the United States where the groundwater contains arsenic concentrations in excess of the Environmental Protection Agency standard of 10 parts per billion adopted in 2001. Millions of private wells have unknown arsenic levels, and in some areas of the US, over 20% of wells may contain levels that are not safe.

Arsine

Arsine is a gas consisting of arsenic and hydrogen. It is extremely toxic to humans, with headaches, vomiting, and abdominal pains occurring within a few hours of exposure. EPA has not classified arsine for carcinogenicity.

Drinking water regulations require public water systems to monitor for arsenic at the entry point to the distribution system. There is no federal requirement for systems to monitor for arsenic within the distribution system. You may, however, want to test your distribution system water for arsenic to be sure that the water being delivered has arsenic levels below the MCL. If you decide to monitor your distribution system, consider testing for arsenic at locations where the settling and accumulation of iron solids or pipe scales are likely (i.e., areas with cast iron pipe, ductile iron pipe, or galvanized iron pipe).

If your water system has installed some form of arsenic treatment, keep in mind that the treatment you installed may change the water quality in other ways. It might cause the water to react differently in the distribution system. Depending on the kind of treatment you've installed, consider what distribution system problems might result.

A change in the taste, odor or appearance of the water at customers' taps may be the first indication of a problem. Some water quality parameters to consider monitoring, depending on your arsenic treatment technology, include iron, pH, manganese, alkalinity, and aluminum.

The current drinking water standard or Maximum Contaminant Level (MCL) set by the U.S. Environmental Protection Agency (EPA) is 0.010 mg/L or parts per million (ppm). This is equivalent to 10 ug/L (micrograms per liter) or 10 ppb. In 2001, the U.S. Environmental Protection Agency (EPA) reduced the regulatory MCL from 50 ppb to 10 ppb on the basis on bladder and lung cancer risks. The MCL is based on the average individual consuming 2 liters of water a day for a lifetime. Long term exposure to drinking water containing arsenic at levels higher than 10 ppb increases the chances of getting cancer, while for lower arsenic water levels the chances are less.

If your water has arsenic levels above 10 ppb, you should obtain drinking water from another source or install a home treatment device. Concentrations above 10 ppb will increase the risk of long-term or chronic health problems, the higher the level and length of exposure, the greater the risk. It is especially important to reduce arsenic water concentrations if you have children or are pregnant. Children are at greater risk (to any agent in water) because of their greater water consumption on a per unit body weight basis. Pregnant women may wish to reduce their arsenic exposures because arsenic has been found at low levels in mother's milk and will cross the placenta, increasing exposures and risks for the fetus. If your water has arsenic levels above 200 ppb, you should immediately stop drinking the water until you can either obtain water from another source or install and maintain treatment.

Physical Characteristics

The three most common arsenic allotropes are *metallic gray*, *yellow* and *black arsenic*, with gray being the most common. *Gray arsenic* (α -As, space group R3m No. 166) adopts a double-layered structure consisting of many interlocked ruffled six-membered rings. Because of weak bonding between the layers, gray arsenic is brittle and has a relatively low Mohs hardness of 3.5. Nearest and next-nearest neighbors form a distorted octahedral complex, with the three atoms in the same double-layer being slightly closer than the three atoms in the next. This relatively close packing leads to a high density of 5.73 g/cm³. Gray arsenic is a semimetal, but becomes a semiconductor with a bandgap of 1.2–1.4 eV if amorphized. *Yellow arsenic* is soft and waxy, and somewhat similar to tetraphosphorus (P₄). Both have four atoms arranged in a tetrahedral structure in which each atom is bound to each of the other three atoms by a single bond. This unstable allotrope, being molecular, is the most volatile, least dense and most toxic. Solid yellow arsenic is produced by rapid cooling of arsenic vapor, As₄. It is rapidly transformed into the gray arsenic by light. The yellow form has a density of 1.97 g/cm³. *Black arsenic* is similar in structure to red phosphorus.

Isotopes

Naturally occurring arsenic is composed of one stable isotope, ⁷⁵As. As of 2003, at least 33 radioisotopes have also been synthesized, ranging in atomic mass from 60 to 92. The most stable of these is ⁷³As with a half-life of 80.3 days. Isotopes that are lighter than the stable ⁷⁵As tend to decay by β^+ decay, and those that are heavier tend to decay by β^- decay, with some exceptions.

At least 10 nuclear isomers have been described, ranging in atomic mass from 66 to 84. The most stable of arsenic's isomers is ^{68m}As with a half-life of 111 seconds.

Chemistry

When heated in air, arsenic oxidizes to arsenic trioxide; the fumes from this reaction have an odor resembling garlic. This odor can be detected on striking arsenide minerals such as arsenopyrite with a hammer. Arsenic (and some arsenic compounds) sublimes upon heating at atmospheric pressure, converting directly to a gaseous form without an intervening liquid state at 887 K (614 °C). The triple point is 3.63 MPa and 1,090 K (820 °C). Arsenic makes arsenic acid with concentrated nitric acid, arsenious acid with dilute nitric acid, and arsenic trioxide with concentrated sulfuric acid.

Compounds

Arsenic compounds resemble in some respects those of phosphorus, which occupies the same group (column) of the periodic table. Arsenic is less commonly observed in the pentavalent state, however. The most common oxidation states for arsenic are: -3 in the arsenides, such as alloy-like intermetallic compounds; and +3 in the arsenites, arsenates (III), and most organoarsenic compounds. Arsenic also bonds readily to itself as seen in the square As₃₋₄ ions in the mineral skutterudite. In the +3 oxidation state, arsenic is typically pyramidal, owing to the influence of the lone pair of electrons.

Inorganic

Arsenic forms colorless, odorless, crystalline oxides As_2O_3 ("white arsenic") and As_2O_5 , which are hygroscopic and readily soluble in water to form acidic solutions. Arsenic (V) acid is a weak acid. Its salts are called arsenates, which is the basis of arsenic contamination of groundwater, a problem that affects many people. Synthetic arsenates include Paris Green (copper(II) acetoarsenite), calcium arsenate, and lead hydrogen arsenate. The latter three have been used as agricultural insecticides and poisons.

The protonation steps between the arsenate and arsenic acid are similar to those between phosphate and phosphoric acid. Unlike phosphorus acid, arsenous acid is genuinely tribasic, with the formula $\text{As}(\text{OH})_3$.

A broad variety of sulfur compounds of arsenic are known. Orpiment (As_2S_3) and realgar (As_4S_4) are somewhat abundant and were formerly used as painting pigments. In As_4S_{10} , arsenic has a formal oxidation state of +2 in As_4S_4 , which features As-As bonds so that the total covalency of As is still three.

The trifluoride, trichloride, tribromide, and triiodide of arsenic (III) are well known, whereas only Arsenic pentafluoride (AsF_5) is the only important pentahalide. Again reflecting the lower stability of the 5+ oxidation state, the pentachloride is stable only below -50°C .

Organoarsenic Compounds

A large variety of organoarsenic compounds are known. Several were developed as chemical warfare agents during World War I, including vesicants such as lewisite and vomiting agents such as adamsite. Cacodylic acid, which is of historic and practical interest, arises from the methylation of arsenic trioxide, a reaction that has no analogy in phosphorus chemistry.

Alloys

Arsenic is used as the group 5 element in the III-V semiconductors gallium arsenide, indium arsenide, and aluminum arsenide. The valence electron count of GaAs is the same as a pair of Si atoms, but the band structure is completely different, which results in distinct bulk properties. Other arsenic alloys include the II-IV semiconductor cadmium arsenide.

Occurrence and Production

Minerals with the formula MAsS and MAs_2 ($\text{M} = \text{Fe}, \text{Ni}, \text{Co}$) are the dominant commercial sources of arsenic, together with realgar (an arsenic sulfide mineral) and native arsenic. An illustrative mineral is arsenopyrite (FeAsS), which is structurally related to iron pyrite. Many minor As-containing minerals are known. Arsenic also occurs in various organic forms in the environment. Inorganic arsenic and its compounds, upon entering the food chain, are progressively metabolized to a less toxic form of arsenic through a process of methylation.

Other naturally occurring pathways of exposure include volcanic ash, weathering of arsenic-containing minerals and ores, and dissolved in groundwater. It is also found in food, water, soil, and air. Arsenic is absorbed by all plants, but is more concentrated in leafy vegetables, rice, apple and grape juice, and seafood. An additional route of exposure is through inhalation.

In 2005, China was the top producer of white arsenic with almost 50% world share, followed by Chile, Peru, and Morocco, according to the British Geological Survey and the United States Geological Survey. Most operations in the US and Europe have closed for environmental reasons. The arsenic is recovered mainly as a side product from the purification of copper. Arsenic is part of the smelter dust from copper, gold, and lead smelters.

On roasting in air of arsenopyrite, arsenic sublimes as arsenic (III) oxide leaving iron oxides, while roasting without air results in the production of metallic arsenic. Further purification from sulfur and other chalcogens is achieved by sublimation in vacuum or in a hydrogen atmosphere or by distillation from molten lead-arsenic mixture.

History

The word "Arsenic" was adopted in Latin *arsenicum* and Old French *arsenic*, from which the English word *arsenic* is derived. Arsenic sulfides (orpiment, realgar) and oxides have been known and used since ancient times. Zosimos (circa 300 AD) describes roasting *sandarach* (realgar) to obtain *cloud of arsenic* (arsenious oxide), which he then reduces to metallic arsenic. As the symptoms of arsenic poisoning were somewhat ill-defined, it was frequently used for murder until the advent of the Marsh test, a sensitive chemical test for its presence. (Another less sensitive but more general test is the Reinsch test.) Owing to its use by the ruling class to murder one another and its potency and discreetness, arsenic has been called the *Poison of Kings* and the *King of Poisons*.

During the Bronze Age, arsenic was often included in bronze, which made the alloy harder (so-called "arsenical bronze"). Albertus Magnus (Albert the Great, 1193–1280) is believed to have been the first to isolate the element from a compound in 1250, by heating soap together with arsenic trisulfide. In 1649, Johann Schröder published two ways of preparing arsenic. Crystals of elemental (native) arsenic are found in nature, although rare. Cadet's fuming liquid (impure cacodyl), often claimed as the first synthetic organometallic compound, was synthesized in 1760 by Louis Claude Cadet de Gassicourt by the reaction of potassium acetate with arsenic trioxide.

In the Victorian era, "arsenic" ("white arsenic" or arsenic trioxide) was mixed with vinegar and chalk and eaten by women to improve the complexion of their faces, making their skin paler to show they did not work in the fields. Arsenic was also rubbed into the faces and arms of women to "improve their complexion". The accidental use of arsenic in the adulteration of foodstuffs led to the Bradford sweet poisoning in 1858, which resulted in approximately 20 deaths.

Health Hazard Information

Arsenic

Arsenic is known to cause cancer, as well as many other serious health problems. Here we review the hazards of arsenic exposure and ways people can protect themselves from these hazards.

Arsenic is an element in the environment that can be found naturally in rocks and soil, water, air, and in plants and animals. It can also be released into the environment from some agricultural and industrial sources.

Arsenic has no taste or smell. Although sometimes found in its pure form as a steel grey metal, arsenic is usually part of chemical compounds. These compounds are divided into 2 groups:

- Inorganic compounds (combined with oxygen, iron, chlorine, and sulfur)
- Organic compounds (combined with carbon and other atoms)

Inorganic arsenic compounds are found in industry, in building products (in some "pressure-treated" woods), and in arsenic-contaminated water. This is the form of arsenic that tends to be more toxic and has been linked to cancer.

Organic arsenic compounds are much less toxic than the inorganic arsenic compounds and are not thought to be linked to cancer. These compounds are found in some foods, such as fish and shellfish.

While arsenic levels may fluctuate over time, what is most significant from the standpoint of cancer risk is long-term exposure.

For water systems in the 25 states that reported arsenic data to the EPA, we have calculated two estimates of average long-term levels: one is a very conservative estimate, the other our best estimate, based on what we believe to be the most reasonable analytical techniques (details on how we arrived at the estimates are included with the charts).

The table below shows the lifetime risks of dying of cancer from arsenic in tap water, based on the National Academy of Sciences' 1999 risk estimates.

Arsenic Level in Tap Water (in parts per billion, or ppb)	Approximate Total Cancer Risk (assuming 2 liters consumed/day)
0.5 ppb	1 in 10,000
1 ppb	1 in 5,000
3 ppb	1 in 1,667
4 ppb	1 in 1,250
5 ppb	1 in 1,000
10 ppb	1 in 500
20 ppb	1 in 250
25 ppb	1 in 200
50 ppb	1 in 100

Arsenic Diabetes

New research findings from the National Health and Nutrition Examination Survey suggest that exposure to levels of arsenic commonly found in drinking water may be a risk factor for type 2 diabetes. The findings suggest that millions of Americans may be at increased risk for type 2 diabetes based on the level of arsenic in their drinking water.

Data on the nearly 800 participants in the study for which urinary arsenic concentrations were available, indicated that urine levels of arsenic were significantly associated with the prevalence of type 2 diabetes. After splitting the subjects into 5 groups based on the level of arsenic in their urine, the researchers determined that those in the highest category were more than three and one-half times more likely to have diabetes. The strength of arsenic as a risk factor for diabetes is similar to other factors such as obesity.

Inorganic arsenic in drinking water at concentrations higher than 100 parts per million has been linked to type 2 diabetes in studies that took place in Taiwan, Mexico, and Bangladesh where drinking water is commonly contaminated with high levels of arsenic. The US drinking water standard is currently 10 parts per million, but most people on private wells have not had their water tested and aren't required to. The researchers estimate that about 13 million Americans live in areas where public water systems exceed the EPA standard for arsenic and this number does not include private wells and water systems.

Animal studies have shown that arsenic affects the production of glucose, insulin secretion and can cause insulin resistance. The current findings reinforce the need to evaluate the role of arsenic in diabetes development in prospective epidemiologic studies conducted in populations exposed to a wide range of arsenic levels.

Acute Effects:**Inorganic Arsenic**

Acute inhalation exposure of workers to high levels of arsenic dusts or fumes has resulted in gastrointestinal effects (nausea, diarrhea, abdominal pain), while acute exposure of workers to inorganic arsenic has also resulted in central and peripheral nervous system disorders.

Acute oral exposure to inorganic arsenic, at doses of approximately 600 micrograms per kilogram body weight per day ($\mu\text{g/kg/d}$) or higher in humans, has resulted in death. Oral exposure to lower levels of inorganic arsenic has resulted in effects on the gastrointestinal tract (nausea, vomiting), central nervous system (CNS) (headaches, weakness, delirium), cardiovascular system (hypotension, shock), liver, kidney, and blood (anemia, leukopenia).

Acute animal tests in rats and mice have shown inorganic arsenic to have moderate to high acute toxicity.

Arsine

Acute inhalation exposure to arsine by humans has resulted in death; it has been reported that a half-hour exposure to 25 to 50 parts per million (ppm) can be lethal.

The major effects from acute arsine exposure in humans include headaches, vomiting, abdominal pains, hemolytic anemia, hemoglobinuria, and jaundice; these effects can lead to kidney failure.

Arsine has been shown to have extreme acute toxicity from acute animal tests.



Chronic Effects (Non-cancer):

Inorganic arsenic

Chronic inhalation exposure to inorganic arsenic in humans is associated with irritation of the skin and mucous membranes (dermatitis, conjunctivitis, pharyngitis, and rhinitis).

Chronic oral exposure to inorganic arsenic in humans has resulted in gastrointestinal effects, anemia, peripheral neuropathy, skin lesions, hyperpigmentation, gangrene of the extremities, vascular lesions, and liver or kidney damage.

No chronic inhalation exposure studies have been performed in animals for any inorganic arsenic compound.

Some studies have suggested that inorganic arsenic is an essential dietary nutrient in goats, chicks, and rats. However, no comparable data are available for humans. EPA has concluded that essentiality, although not rigorously established, is plausible.

EPA has not established a Reference Concentration (RfC) for inorganic arsenic.

The California Environmental Protection Agency (CalEPA) has established a chronic inhalation reference level of 0.00003 milligrams per cubic meter (mg/m^3) based on developmental effects in mice. The CalEPA reference exposure level is a concentration at or below which adverse health effects are not likely to occur. It is not a direct estimator of risk, but rather a reference point to gauge the potential effects. At lifetime exposures increasingly greater than the reference exposure level, the potential for adverse health effects increases.

The Reference Dose (RfD) for inorganic arsenic is 0.0003 milligrams per kilogram body weight per day ($\text{mg}/\text{kg}/\text{d}$) based on hyperpigmentation, keratosis, and possible vascular complications in humans. The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer effects during a lifetime.

EPA has medium confidence in the study on which the RfD for inorganic arsenic was based because, although an extremely large number of people were included in the assessment (>40,000), the doses were not well characterized and other contaminants were present. The supporting human toxicity database, while extensive, is somewhat flawed and, consequently, EPA has assigned medium confidence to the RfD.

Arsine

No information is available on the chronic effects of arsine in humans.

The RfC for arsine is 0.00005 mg/m³ based on increased hemolysis, abnormal red blood cell morphology, and increased spleen weight in rats, mice, and hamsters.

EPA has medium confidence in the RfC based on: (1) high confidence in the studies on which the RfC for arsine was based because the sample sizes were adequate, statistical significance was reported, concentration dose-response relationships were documented, three species were investigated, and both a no-observed-adverse-effect level (NOAEL) and a lowest-observed-adverse-effect level (LOAEL) were identified, and (2) medium confidence in the database because while there were three inhalation animal studies and a developmental/reproductive study, there were no data available on human exposure.

Reproductive/Developmental Effects:

Inorganic arsenic

Several studies have suggested that women who work in, or live near, metal smelters may have higher than normal spontaneous abortion rates, and their children may exhibit lower than normal birth weights. However, these studies are limited because they were designed to evaluate the effects of smelter pollutants in general, and are not specific for inorganic arsenic.

Ingested inorganic arsenic can cross the placenta in humans, exposing the fetus to the chemical.

Oral animal studies have reported inorganic arsenic at very high doses to be fetotoxic and to cause birth defects.

Arsine

Human studies have indicated higher than expected spontaneous abortion rates in women in the microelectronics industry who were exposed to arsine. However, these studies have several limitations, including small sample size and exposure to other chemicals in addition to arsine.

Cancer Risk:

Inorganic arsenic

Human, inhalation studies have reported inorganic arsenic exposure to be strongly associated with lung cancer.

Ingestion of inorganic arsenic in humans has been associated with an increased risk of nonmelanoma skin cancer and also to an increased risk of bladder, liver, and lung cancer.

Animal studies have not associated inorganic arsenic exposure via the oral route with cancer, and no cancer inhalation studies have been performed in animals for inorganic arsenic.

EPA has classified inorganic arsenic as a Group A, human carcinogen.

EPA used a mathematical model, using data from an occupational study of arsenic-exposed copper smelter workers, to estimate the probability of a person developing cancer from continuously breathing air containing a specified concentration of inorganic arsenic. EPA calculated an inhalation unit risk estimate of $4.3 \times 10^{-3}(\mu\text{g}/\text{m}^3)^{-1}$. EPA estimates that, if an individual were to continuously breathe air containing inorganic arsenic at an average of $0.0002 \mu\text{g}/\text{m}^3$ ($2 \times 10^{-7} \text{ mg}/\text{m}^3$) over his or her entire lifetime, that person would theoretically have no more than a one-in-a-million increased chance of developing cancer as a direct result of breathing air containing this chemical. Similarly, EPA estimates that continuously breathing air containing $0.002 \mu\text{g}/\text{m}^3$ ($2 \times 10^{-6} \text{ mg}/\text{m}^3$) would result in not greater than a one-in-a-hundred thousand increased chance of developing cancer, and air containing $0.02 \mu\text{g}/\text{m}^3$ ($2 \times 10^{-5} \text{ mg}/\text{m}^3$) would result in not greater than a one-in-ten thousand increased chance of developing cancer. For a detailed discussion of confidence in the potency estimates, please see IRIS.

EPA has calculated an oral cancer slope factor of $1.5 (\text{mg}/\text{kg}/\text{d})^{-1}$ for inorganic arsenic.

Arsine

No cancer inhalation studies in humans or animals are available for arsine.

EPA has not classified arsine for carcinogenicity.

Physical Properties

Inorganic arsenic is a naturally occurring element in the earth's crust.

Pure inorganic arsenic is a gray-colored metal, but inorganic arsenic is usually found combined with other elements such as oxygen, chlorine, and sulfur.

The chemical symbol for inorganic arsenic is As, and it has an atomic weight of 74.92 g/mol.

The chemical formula for arsine is AsH_3 , and it has a molecular weight of 77.95 g/mol.

Arsine is a colorless gas with a disagreeable garlic odor.

Arsenic combined with elements such as oxygen, chlorine, and sulfur forms inorganic arsenic; inorganic arsenic compounds include arsenic pentoxide, arsenic trioxide, and arsenic acid. Arsenic combined with carbon and hydrogen forms organic arsenic; organic arsenic compounds include arsanilic acid, arsenobetaine, and dimethylarsinic acid.

Arsenic Applications

Agricultural

The toxicity of arsenic to insects, bacteria and fungi led to its use as a wood preservative. In the 1950s a process of treating wood with chromated copper arsenate (also known as CCA or Tanalith) was invented, and for decades this treatment was the most extensive industrial use of arsenic. An increased appreciation of the toxicity of arsenic resulted in a ban for the use of CCA in consumer products; the European Union and United States initiated this process in 2004. CCA remains in heavy use in other countries however, e.g. Malaysian rubber plantations.

Arsenic was also used in various agricultural insecticides, termination and poisons. For example, lead hydrogen arsenate was a common insecticide on fruit trees, but contact with the compound sometimes resulted in brain damage among those working the sprayers. In the second half of the 20th century, monosodium methyl arsenate (MSMA) and disodium methyl arsenate (DSMA) – less toxic organic forms of arsenic – have replaced lead arsenate in agriculture.

Arsenic is still added to animal food, in particular in the US as a method of disease prevention and growth stimulation. One example is roxarsone, which is used as a broiler starter by about 70% of the broiler growers since 1995. The Poison-Free Poultry Act of 2009 proposes to ban the use of roxarsone in industrial swine and poultry production. Alpharma, a subsidiary of Pfizer Inc., which produces Roxarsone, has voluntarily suspended sales of the drug in response to studies showing elevated levels of arsenic in treated chickens.

Medical use

During the 18th, 19th, and 20th centuries, a number of arsenic compounds have been used as medicines, including arsphenamine (by Paul Ehrlich) and arsenic trioxide (by Thomas Fowler). Arsphenamine as well as neosalvarsan was indicated for syphilis and trypanosomiasis, but has been superseded by modern antibiotics. Arsenic trioxide has been used in a variety of ways over the past 500 years, but most commonly in the treatment of cancer. The US Food and Drug Administration in 2000 approved this compound for the treatment of patients with acute promyelocytic leukemia that is resistant to ATRA.

It was also used as Fowler's solution in psoriasis. Recently new research has been done in locating tumors using arsenic-74 (a positron emitter). The advantages of using this isotope instead of the previously used iodine-124 is that the signal in the PET scan is clearer as the body tends to transport iodine to the thyroid gland producing a lot of noise. In subtoxic doses, soluble arsenic compounds act as stimulants, and were once popular in small doses as medicine by people in the mid-18th century.

Alloys

The main use of metallic arsenic is for alloying with lead. Lead components in car batteries are strengthened by the presence of a few percent of arsenic. Dezincification can be strongly reduced by adding arsenic to brass, a copper-zinc alloy. Gallium arsenide is an important semiconductor material, used in integrated circuits.

Circuits made from GaAs are much faster (but also much more expensive) than those made in silicon. Unlike silicon it has a direct bandgap, and so can be used in laser diodes and LEDs to directly convert electricity into light.

Military

After World War I, the United States built up a stockpile of 20,000 tons of lewisite ($\text{ClCH}=\text{CHAsCl}_2$), a chemical weapon that is a vesicant (blister agent) and lung irritant. The stockpile was neutralized with bleach and dumped into the Gulf of Mexico after the 1950s. During the Vietnam War the United States used Agent Blue, a mixture of sodium cacodylate and its acid form, as one of the rainbow herbicides to deprive invading North Vietnamese soldiers of foliage cover and rice.

Other uses

- Copper acetoarsenite was used as a green pigment known under many names, including 'Paris Green' and 'Emerald Green'. It caused numerous arsenic poisonings. Scheele's Green, a copper arsenate, was used in the 19th century as a coloring agent in sweets.
- Also used in bronzing and pyrotechnics.
- Up to 2% of arsenic is used in lead alloys for lead shots and bullets.
- Arsenic is added in small quantities to alpha-brass to make it dezincification resistant. This grade of brass is used to make plumbing fittings or other items that are in constant contact with water.
- Arsenic is also used for taxonomic sample preservation.
- Until recently arsenic was used in optical glass. Modern glass manufacturers, under pressure from environmentalists, have removed it, along with lead.

Bacteria

Some species of bacteria obtain their energy by oxidizing various fuels while reducing arsenate to arsenite. Under oxidative environmental conditions some bacteria use arsenite, which is oxidized to arsenate as fuel for their metabolism. The enzymes involved are known as arsenate reductases (Arr).

In 2008, bacteria were discovered that employ a version of photosynthesis in the absence of oxygen with arsenites as electron donors, producing arsenates (just as ordinary photosynthesis uses water as electron donor, producing molecular oxygen). Researchers conjecture that, over the course of history, these photosynthesizing organisms produced the arsenates that allowed the arsenate-reducing bacteria to thrive. One strain PHS-1 has been isolated and is related to the Gammaproteobacterium *Ectothiorhodospira shaposhnikovii*.

The mechanism is unknown, but an encoded Arr enzyme may function in reverse to its known homologues. Although the arsenate and phosphate anions are similar structurally, no evidence exists for the replacement of phosphate in ATP or nucleic acids by arsenic.

It is known that even if your water has detectable levels of arsenic that are below the 0.010 mg/L MCL, and you have iron pipes or components in your distribution system, your system's pipes may have arsenic-rich scales attached to them. As long as the scales are not disturbed, they will remain attached to the pipes or other distribution system components. Certain conditions, such as flushing of mains or fire flow conditions, may result in those scales being sloughed off and suspended in the water, releasing the arsenic. Other conditions, such as changes in water chemistry, may result in some of the arsenic dissolving back into the water. Both of these situations could cause high arsenic levels at consumers' taps.

Arsenic Control Measures Can Affect Finished Water Quality

Public water systems installing arsenic treatment should be informed about possible changes to their finished water that may result from the arsenic treatment they install. For example, systems may need to adjust their finished water quality to address new concerns about corrosion. Changes in water chemistry due to using new sources, blending different source waters, or installing arsenic treatment are some of the factors that can affect distribution system water quality. In some cases, this may cause an increase in arsenic levels in the distribution system or create simultaneous compliance issues with other drinking water regulations.

Water systems may also find deposits of arsenic-rich particles in their storage tanks or at locations in their distribution system with low flows. If the flow is increased or a storage tank is drawn down to a low level, these arsenic-rich particles can get stirred up and transported to consumers' taps. This situation occurs primarily when iron media used in treatment are released into the distribution system, or when iron particles are not properly filtered out during iron removal treatment. If these treatment technologies are operated correctly, this should not be a problem for most water systems.

Is Arsenic in your Storage Tank?

Is Your Ground Water System Installing Disinfection for Pathogen Control?

Water systems that disinfect their water should be aware of the possibility of an increase in arsenic concentrations in their distribution system, particularly if the water contains high concentrations of dissolved iron. When chlorinated, the dissolved iron forms particles on which arsenic can accumulate. As a result, high arsenic concentrations may occur in distribution system water even if arsenic concentrations in the raw water are below the MCL.

This happened to a small community water system in the Midwest that began chlorinating water from a series of wells that had raw water arsenic levels between 0.003 and 0.008 mg/L and iron concentrations up to 0.4 mg/L. At the same time, the system installed a polyphosphate feed system for corrosion control. Soon after chlorination began, the system received intermittent colored-water complaints from its customers with increasing frequency across the distribution system.

Samples collected from several representative locations throughout the service area had a reddish-brown color and contained particles. A metals analysis showed high levels of copper and iron oxides in the finished water, along with arsenic concentrations approaching 5 mg/L. Because of the water's colored appearance, it was considered unlikely that customers would consume the water.

Doctors and health care professionals were notified of the situation and instructed to watch for signs of arsenic poisoning.

Researchers found that chlorinating the water caused the formation of ferri-hydroxide solids. The minimal arsenic present in the groundwater was being concentrated as it absorbed onto the solids. Copper oxide particulates also formed and were released. To some extent, the polyphosphates served a useful role by keeping iron in solution and counteracting the tendency for the iron oxides to form, but additional steps were needed. For six months the system alternated their chlorination schedule: on for one day then off two days. The system then returned to full-time chlorination, starting with a low distribution system residual of 0.2 mg/L and gradually increasing it to 0.5 mg/L. The system continued to flush water mains on a semi-annual schedule using a unidirectional approach. In the last year, the system received only one colored water complaint.

Heredity

Arsenic has been linked to epigenetic changes, heritable changes in gene expression that occur without changes in DNA sequence. These include DNA methylation, histone modification, and RNA interference. Toxic levels of arsenic cause significant DNA hypermethylation of tumor suppressor genes p16 and p53, thus increasing risk of carcinogenesis.

These epigenetic events have been studied *in vitro* using human kidney cells and *in vivo* using rat liver cells and peripheral blood leukocytes in humans. Inductive coupled plasma mass spectrometry (ICP-MS) is used to detect precise levels of intracellular arsenic and its other bases involved in epigenetic modification of DNA. Studies investigating arsenic as an epigenetic factor will help in developing precise biomarkers of exposure and susceptibility.

The Chinese brake fern (*Pteris vittata*) hyperaccumulates arsenic present in the soil into its leaves and has a proposed use in phytoremediation.

Biomethylation

Inorganic arsenic and its compounds, upon entering the food chain, are progressively metabolized through a process of methylation. For example, the mold *Scopulariopsis brevicaulis* produce significant amounts of trimethylarsine if inorganic arsenic is present. The organic compound arsenobetaine is found in some marine foods such as fish and algae, and also in mushrooms in larger concentrations. The average person's intake is about 10–50 µg/day. Values about 1000 µg are not unusual following consumption of fish or mushrooms, but there is little danger in eating fish because this arsenic compound is nearly non-toxic.

Arsenic Environmental Issues

Arsenic Control Measures Can Affect Finished Water Quality

Public water systems installing arsenic treatment should be informed about possible changes to their finished water that may result from the arsenic treatment they install. For example, systems may need to adjust their finished water quality to address new concerns about corrosion. Changes in water chemistry due to using new sources, blending different source waters, or installing arsenic treatment are some of the factors that can affect distribution system water quality. In some cases, this may cause an increase in arsenic levels in the distribution system or create simultaneous compliance issues with other drinking water regulations.

Occurrence in drinking water

Widespread arsenic contamination of groundwater has led to a massive epidemic of arsenic poisoning in Bangladesh and neighboring countries. It is estimated that approximately 57 million people in the Bengal basin are drinking groundwater with arsenic concentrations elevated above the World Health Organization's standard of 10 parts per billion (ppb). However, a study of cancer rates in Taiwan suggested that significant increases in cancer mortality appear only at levels above 150 ppb.

The arsenic in the groundwater is of natural origin, and is released from the sediment into the groundwater, owing to the anoxic conditions of the subsurface. This groundwater began to be used after local and western NGOs and the Bangladeshi government undertook a massive shallow tube well drinking-water program in the late twentieth century.

This program was designed to prevent drinking of bacteria-contaminated surface waters, but failed to test for arsenic in the groundwater. Many other countries and districts in Southeast Asia, such as Vietnam and Cambodia have geological environments conducive to generation of high-arsenic groundwaters. Arsenicosis was reported in Nakhon Si Thammarat, Thailand in 1987, and the dissolved arsenic in the Chao Phraya River is suspected of containing high levels of naturally occurring arsenic, but has not been a public health problem owing to the use of bottled water.

In the United States, arsenic is most commonly found in the ground waters of the southwest. Parts of New England, Michigan, Wisconsin, Minnesota and the Dakotas are also known to have significant concentrations of arsenic in ground water. Increased levels of skin cancer have been associated with arsenic exposure in Wisconsin, even at levels below the 10 part per billion drinking water standard, although this link has not been proven. According to a recent film funded by the US Superfund, millions of private wells have unknown arsenic levels, and in some areas of the US, over 20% of wells may contain levels that exceed established limits.

Low-level exposure to arsenic at concentrations found commonly in US drinking water compromises the initial immune response to H1N1 or swine flu infection according to NIEHS-supported scientists. The study, conducted in laboratory mice, suggests that people exposed to arsenic in their drinking water may be at increased risk for more serious illness or death in response to infection from the virus.

Some Canadians are drinking water that contains inorganic arsenic. Private dug well waters are most at risk for containing inorganic arsenic. Preliminary well water analyses typically does not test for arsenic. Researchers at the Geological Survey of Canada have modeled relative variation in natural arsenic hazard potential for the province of New Brunswick. This study has important implications for potable water and health concerns relating to inorganic arsenic.

Epidemiological evidence from Chile shows a dose-dependent connection between chronic arsenic exposure and various forms of cancer, in particular when other risk factors, such as cigarette smoking, are present. These effects have been demonstrated to persist below 50 ppb.

Analyzing multiple epidemiological studies on inorganic arsenic exposure suggests a small but measurable risk increase for bladder cancer at 10 ppb. According to Peter Ravenscroft of the Department of Geography at the University of Cambridge, roughly 80 million people worldwide consume between 10 and 50 ppb arsenic in their drinking water. If they all consumed exactly 10 ppb arsenic in their drinking water, the previously cited multiple epidemiological study analysis would predict an additional 2,000 cases of bladder cancer alone. This represents a clear underestimate of the overall impact, since it does not include lung or skin cancer, and explicitly underestimates the exposure. Those exposed to levels of arsenic above the current WHO standard should weigh the costs and benefits of arsenic remediation.

Early (1973) evaluations of the removal of dissolved arsenic by drinking water treatment processes demonstrated that arsenic is very effectively removed by co-precipitation with either iron or aluminum oxides. The use of iron as a coagulant, in particular, was found to remove arsenic with efficiencies exceeding 90%.

Several adsorptive media systems have been approved for point-of-service use in a study funded by the United States Environmental Protection Agency (US EPA) and the National Science Foundation (NSF). A team of European and Indian scientists and engineers have set up six arsenic treatment plants in West Bengal based on in-situ remediation method (SAR Technology). This technology does not use any chemicals and arsenic is left as an insoluble form (+5 state) in the subterranean zone by recharging aerated water into the aquifer and thus developing an oxidation zone to support arsenic oxidizing micro-organisms. This process does not produce any waste stream or sludge and is relatively cheap.

Another effective and inexpensive method to remove arsenic from contaminated well water is to sink wells 500 feet or deeper to reach purer waters. A recent 2011 study funded by the US National Institute of Environmental Health Sciences' Superfund Research Program shows that deep sediments can remove arsenic and take it out of circulation.

Through this process called adsorption in which arsenic sticks to the surfaces of deep sediment articles, arsenic can be naturally removed from well water.

Magnetic separations of arsenic at very low magnetic field gradients have been demonstrated in point-of-use water purification with high-surface-area and monodisperse magnetite (Fe_3O_4) nanocrystals. Using the high specific surface area of Fe_3O_4 nanocrystals the mass of waste associated with arsenic removal from water has been dramatically reduced.

Epidemiological studies have suggested a correlation between chronic consumption of drinking water contaminated with arsenic and the incidence of all leading causes of mortality. The literature provides reason to believe arsenic exposure is causative in the pathogenesis of diabetes.

Hungarian engineer László Schremmer has recently discovered that by the use of chaff-based filters it is possible to reduce the arsenic content of water to 3 $\mu\text{g/L}$. This is especially important in areas where the potable water is provided by filtering the water extracted from the underground aquifer.

Wood Preservation in the US

As of 2002, US-based industries consumed 19,600 metric tons of arsenic. Ninety percent of this was used for treatment of wood with chromated copper arsenate (CCA). In 2007, 50% of the 5,280 metric tons of consumption was still used for this purpose. In the United States, the use of arsenic in consumer products was discontinued for residential and general consumer construction on December 31, 2003 and alternative chemicals are now used, such as Alkaline Copper Quaternary, borates, copper azole, cyproconazole, and propiconazole.

Although discontinued, this application is also one of the most concerns to the general public. The vast majority of older pressure-treated wood was treated with CCA. CCA lumber is still in widespread use in many countries, and was heavily used during the latter half of the 20th century as a structural and outdoor building material. Although the use of CCA lumber was banned in many areas after studies showed that arsenic could leach out of the wood into the surrounding soil (from playground equipment, for instance), a risk is also presented by the burning of older CCA timber. The direct or indirect ingestion of wood ash from burnt CCA lumber has caused fatalities in animals and serious poisonings in humans; the lethal human dose is approximately 20 grams of ash. Scrap CCA lumber from construction and demolition sites may be inadvertently used in commercial and domestic fires. Protocols for safe disposal of CCA lumber do not exist evenly throughout the world; there is also concern in some quarters about the widespread landfill disposal of such timber.

Water Purification Solutions

Small-scale water treatment

A review of methods to remove arsenic from groundwater in Pakistan summarizes the most technically viable inexpensive methods. A simpler and less expensive form of arsenic removal is known as the Sono arsenic filter, using three pitchers containing cast iron turnings and sand in the first pitcher and wood activated carbon and sand in the second. Plastic buckets can also be used as filter containers. It is claimed that thousands of these systems are in use and can last for years while avoiding the toxic waste disposal problem inherent to conventional arsenic removal plants. Although novel, this filter has not been certified by any sanitary standards such as NSF, ANSI, WQA and does not avoid toxic waste disposal similar to any other iron removal process.

In the United States small "under the sink" units have been used to remove arsenic from drinking water. This option is called "point of use" treatment. The most common types of domestic treatment use the technologies of adsorption (using media such as Bayoxide E33, GFH, or titanium dioxide) or reverse osmosis. Ion exchange and activated alumina have been considered but not commonly used.

Arsenic Large-scale water treatment

In some places, such as the United States, all the water supplied to residences by utilities must meet primary (health-based) drinking water standards. Regulations may necessitate large-scale treatment systems to remove arsenic from the water supply. The effectiveness of any method depends on the chemical makeup of a particular water supply. The aqueous chemistry of arsenic is complex, and may affect the removal rate that can be achieved by a particular process.

Some large utilities with multiple water supply wells could shut down those wells with high arsenic concentrations, and produce only from wells or surface water sources that meet the arsenic standard. Other utilities, however, especially small utilities with only a few wells, may have no available water supply that meets the arsenic standard.

Coagulation/filtration (also known as flocculation) removes arsenic by coprecipitation and adsorption using iron coagulants. Coagulation/filtration using alum is already used by some utilities to remove suspended solids and may be adjusted to remove arsenic. But the problem of this type of filtration system is that it gets clogged very easily, mostly within two to three months. The toxic arsenic sludge are disposed of by concrete stabilization, but there is no guarantee that they won't leach out in future.

Iron oxide adsorption filters the water through a granular medium containing ferric oxide. Ferric oxide has a high affinity for adsorbing dissolved metals such as arsenic. The iron oxide medium eventually becomes saturated, and must be replaced. The sludge disposal is a problem here too.

Activated alumina is an adsorbent that effectively removes arsenic. Activated alumina columns connected to shallow tube wells in India and Bangladesh have successfully removed both As(III) and As(V) from groundwater for decades. Long-term column performance has been possible through the efforts of community-elected water committees that collect a local water tax for funding operations and maintenance. It has also been used to remove undesirably high concentrations of fluoride.

Ion Exchange has long been used as a water-softening process, although usually on a single-home basis. Traditional anion exchange is effective in removing As(V), but not As(III), or arsenic trioxide, which doesn't have a net charge. Effective long-term ion exchange removal of arsenic requires a trained operator to maintain the column.

Both **Reverse osmosis** and **electrodialysis** (also called *electrodialysis reversal*) can remove arsenic with a net ionic charge. (Note that arsenic oxide, As_2O_3 , is a common form of arsenic in groundwater that is soluble, but has no net charge.) Some utilities presently use one of these methods to reduce total dissolved solids and therefore improve taste. A problem with both methods is the production of high-salinity waste water, called brine, or concentrate, which then must be disposed of.

Subterranean Arsenic Removal (SAR) Technology

In subterranean arsenic removal (SAR), aerated groundwater is recharged back into the aquifer to create an oxidation zone which can trap iron and arsenic on the soil particles through adsorption process. The oxidation zone created by aerated water boosts the activity of the arsenic-oxidizing microorganisms which can oxidize arsenic from +3 to +5 state SAR Technology.

No chemicals are used and almost no sludge is produced during operational stage since iron and arsenic compounds are rendered inactive in the aquifer itself. Thus toxic waste disposal and the risk of its future mobilization is prevented. Also, it has very long operational life, similar to the long lasting tube wells drawing water from the shallow aquifers.

Six such SAR plants, funded by the World Bank and constructed by Ramakrishna Vivekananda Mission, Barrackpore & Queen's University Belfast, UK are operating in West Bengal. Each plant has been delivering more than 3,000 liters of arsenic and iron-free water daily to the rural community. The first community water treatment plant based on SAR technology was set up at Kashimpore near Kolkata in 2004 by a team of European and Indian engineers led by Dr. Bhaskar Sen Gupta of Queen's University Belfast for TiPOT.

SAR technology had been awarded Dhirubhai Ambani Award, 2010 from IChemE UK for Chemical Innovation. Again, SAR was the winner of the St. Andrews Award for Environment, 2010. The SAR Project was selected by the Blacksmith Institute - New York & Green Cross- Switzerland as one of the "12 Cases of Cleanup & Success" in the World's Worst Polluted Places Report 2009.

The Hungarian Solution

Hungarian engineer László Schremmer has recently discovered that by the use of chaff-based filters it is possible to reduce the arsenic content of water to 3 microgram/liter. This is especially important in areas where the potable water is provided by filtering the water extracted from the underground aquifer.

Arsenic Can Build Up on and Release in Pipes and Storage Tanks

Water systems may also find deposits of arsenic-rich particles in their storage tanks or at locations in their distribution system with low flows. If the flow is increased or a storage tank is drawn down to a low level, these arsenic-rich particles can get stirred up and transported to consumers' taps. This situation occurs primarily when iron media used in treatment are released into the distribution system, or when iron particles are not properly filtered out during iron removal treatment. If these treatment technologies are operated correctly, this should not be a problem for most water systems.

Public water systems with arsenic in their raw water may find that scales on pipes and other components in their distribution systems contain relatively high arsenic concentrations. These arsenic-rich scales can become dislodged and suspended in the water, and may be ultimately delivered to consumers. Arsenic has been shown to attach to iron in distribution system pipes. Because iron is so effective at binding with arsenic, corrosion deposits can have high concentrations of arsenic solids. In a recent study, arsenic levels found in solids that were collected after pipe sections and hydrants were flushed were as high as 13.65 milligrams of arsenic per gram of solid.

EPA History of Arsenic Section

Fact Sheet on the Arsenic Rule October 31, 2001

EPA ANNOUNCES ARSENIC STANDARD FOR DRINKING WATER OF 10 PARTS PER BILLION

What is the EPA announcing?

The EPA affirms the appropriateness of a maximum contaminant level (**MCL**) (or regulatory level) of 10 parts per billion (ppb) for arsenic in drinking water. Today's announcement will provide additional protection to at least 13 million Americans from cancer and other health problems.

Why did the EPA delay and review the 10ppb standard adopted in January 2001?

The EPA's responsibility is to establish protective health standards in which the public has confidence. Because of the debate surrounding the appropriateness and the cost of the 10 ppb standard (particularly for small water systems), the Administrator sought additional independent expert reviews of the January 2001 regulation.

What are the benefits of setting the standard at 10ppb?

Reducing arsenic from 50 ppb to 10ppb will prevent:

- more than 19-31 cases of bladder cancer per year, prevent 5-8 deaths each year from this cancer,
- more than 19-25 cases of lung cancer, prevent 16-22 deaths from this cancer, and
- a number of cases of non-cancerous diseases, such as heart disease.

How many water systems are affected by this standard?

Of the 74,000 systems regulated by this MCL, approximately 4,000 systems will have to install treatment or take other steps to comply with the 10 ppb standard.

How much will it cost to implement this standard?

The EPA estimates that the average annual household water bill may increase by \$32 per year, however, for households in systems that serve less than 3,300 people the cost will be substantially higher (ranging from \$58 - \$327 per household).

When must water systems meet the 10 ppb standard?

Water systems had to meet this standard by January 23, 2006.

What is EPA doing to help smaller systems meet the 2006 compliance date?

The EPA has planned to provide up to \$20 million since 2006 for research and development of more cost-effective technologies to help small systems meet the more protective 10 ppb standard. The EPA also will provide technical assistance and training to operators of small systems, which will reduce their compliance costs.

Since 1996, states have provided more than \$3.8 in loan assistance through the Drinking Water State Revolving Fund (**DWSRF**) to help water systems improve their infrastructure.

The EPA also provides funding to States for their drinking water programs (including assistance to small systems for control of arsenic) through the Public Water Systems Supervision grants program. Other federal funds are available through Housing and

Urban Development's Community Development Block Grant Program, and the Rural Utilities Service of the U.S. Department of Agriculture.

What are the Consumer Confidence Report (CCR) requirements for arsenic after the effective date of this rule?

Community water systems are required to publish annual reports with information on water source, treatment, and any detected contaminants by July 1 of each year. Under the arsenic rule, systems that detect arsenic between 10 and 50 ppb must include health effects information in the CCR. Systems that detect arsenic between 5 and 10 ppb must include an educational statement in the CCR.

Systems with arsenic concentrations above 50 ppb (in violation of the existing standard) continue to be required to state they are in violation and must provide health effects information.

When are States required to update their programs for the new Arsenic standard?

Under the Safe Drinking Water Act, States have two years after promulgation to submit a complete and final primacy revision application to the EPA. States may request an extension of up to two additional years for program updates. The EPA will grant extensions on a case-by-case basis, depending on need.

For the arsenic standard, the initial two-year period ended on January 22, 2003.

An extension for the entire two-year period ended back on January 22, 2005.

For More Information

For general information on arsenic in drinking water, contact the Safe Drinking Water Hotline, at (800) 426-4791, or visit the EPA Safewater website at <http://www.epa.gov/safewater> or the arsenic website at <http://www.epa.gov/safewater/arsenic.html> on the Internet.



One symptom of Arsenic poisoning from drinking water.

Arsenic Rule

EPA 815-F-00-016

January 2001

1. What are we announcing?

Today's final rule revises the current Maximum Contaminant Level (**MCL**) from 50 µg/L to 10 µg/L and sets a Maximum Contaminant Level Goal (**MCLG**) of zero for arsenic in drinking water. In addition, this final rule also clarifies how compliance is demonstrated for many inorganic and organic contaminants in drinking water.

2. What are the requirements of this final rule?

Both community water systems (**CWSs**) and non-transient, non-community water systems (**NTNCWSs**) will be required to reduce the arsenic concentration in their drinking water systems to 10 g/L.

A CWS is a public water system that serves at least 15 locations or 25 residents regularly year round (e.g., most cities and towns, apartments, and mobile home parks with their own water supplies). An NTNCWS is a public water system that is not a CWS and serves at least 25 of the same people more than 6 months of the year (e.g., schools, churches, nursing homes, and factories).

This final rule is also a vehicle for clarifying two compliance requirements for inorganic contaminants (**IOCs**), volatile organic contaminants (**VOCs**), and synthetic organic contaminants (**SOCs**). When a system fails to collect the required number of samples, compliance averages will be based on the actual number of samples collected. Also, new public water systems and systems using new sources of water must demonstrate compliance within State-specified time and sampling frequencies.

3. How soon after publishing the final rule will the changes take effect?

All CWSs and all NTNCWSs that exceed the MCL of 10 µg/L will be required to come into compliance 5 years after the promulgation of the final rule. Beginning with reports that were due by July 1, 2002, all CWSs will begin providing health information and arsenic concentrations in their annual consumer confidence report (**CCR**) for water that exceeds ½ the revised MCL.

4. Why is this rule significant?

In the 1996 amendments to the Safe Drinking Water Act (**SDWA**), Congress directed the EPA to propose a new arsenic regulation by January 1, 2000 and to issue the final rule by January 1, 2001 (Congress subsequently extended the final rule date to June 22, 2001). EPA published the proposed rule for arsenic on June 22, 2000. The rule proposed an MCL of 5 µg/L for arsenic and the EPA took comment on regulatory options of 3 µg/L (the feasible level), 10 µg/L and 20 µg/L.

The 1996 amendments to SDWA added discretionary authority for the EPA Administrator to adjust the maximum contaminant level (**MCL**) if the benefits would not justify the costs (1412(b)(6)). Today's rule is important because it is the second drinking water regulation in which the EPA will use the discretionary authority under SDWA Section 1412(b)(6). After careful consideration of the benefits and the costs, the EPA has decided to set the drinking water standard for arsenic higher than the technically feasible level of 3 µg/L because the EPA believes that the costs would not justify the

benefits at this level. The EPA believes that the final MCL of 10 µg/L maximizes health risk reduction at a cost justified by the benefits.

5. What health effects are associated with exposure to arsenic from drinking water?

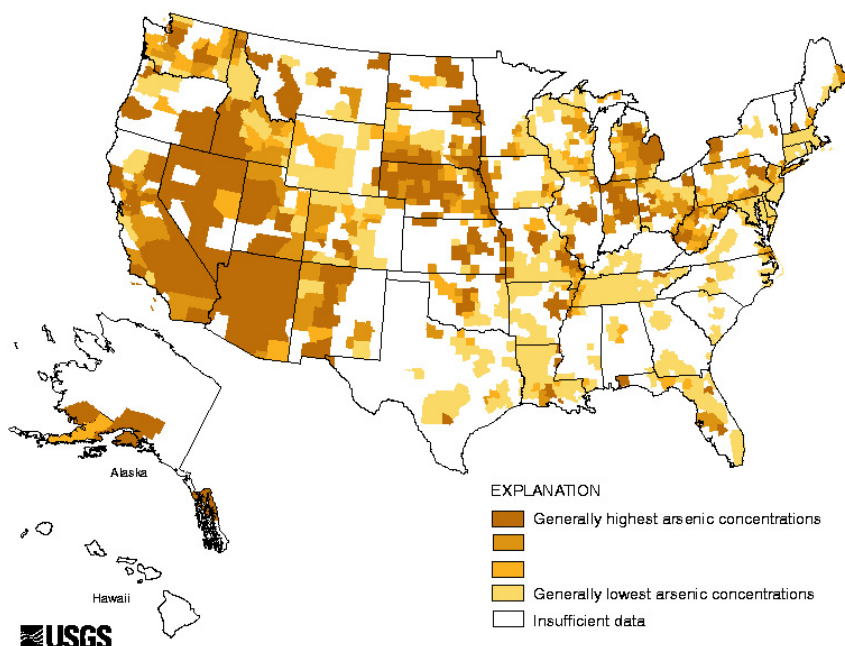
In most drinking water sources, the inorganic form of arsenic tends to be more predominant than organic forms. Inorganic arsenic in drinking water can exert toxic effects after acute (short-term) or chronic (long-term) exposure. Although acute exposures to high doses of inorganic arsenic can cause adverse effects, such exposures do not occur from public water systems in the U.S. that are in compliance with the existing MCL of 50 µg/L.

Today's final rule addresses the long-term, chronic effects of exposure to low concentrations of inorganic arsenic in drinking water. Studies link inorganic arsenic ingestion to a number of health effects. **These health effects include:**

- **Cancerous Effects:** skin, bladder, lung, kidney, nasal passages, liver and prostate cancer; and
- **Non-cancerous effects:** cardiovascular, pulmonary, immunological, neurological and endocrine (e.g., diabetes) effects.

6. What are the sources of arsenic contamination in water?

The contamination of a drinking water source by arsenic can result from either natural or human activities. Arsenic is an element that occurs naturally in rocks and soil, water, air, plants, and animals. Volcanic activity, the erosion of rocks and minerals, and forest fires are natural sources that can release arsenic into the environment. Although about 90 percent of the arsenic used by industry in the United States is currently used for wood preservative purposes, arsenic is also used in paints, drugs, dyes, soaps, metals and semi-conductors. Agricultural applications, mining, and smelting also contribute to arsenic releases.



7. How many people and how many systems will be affected by this rule?

Higher levels of arsenic tend to be found more in ground water sources than in surface water sources (i.e., lakes and rivers) of drinking water. Compared to the rest of the United States, the Western states have more systems with arsenic levels greater than 10 µg/L.

Parts of the Midwest and New England have some systems whose current arsenic levels are greater than 10 µg/L, but more systems with arsenic levels that range from 2-10 µg/L of arsenic.

While many systems may not have detected arsenic in their drinking water above 10 µg/L, there may be geographic "**hot spots**" with systems that may have higher levels of arsenic than the predicted occurrence for that area.

About 3,000 (or 5.5 percent) of the nation's 54,000 CWSs and 1,100 (or 5.5 percent) of the 20,000 NTNCWSs will need to take measures to lower arsenic in their drinking water. Of the affected systems, 97 percent serve less than 10,000 people.

Arsenic Guidance August 2002 Appendix N-9

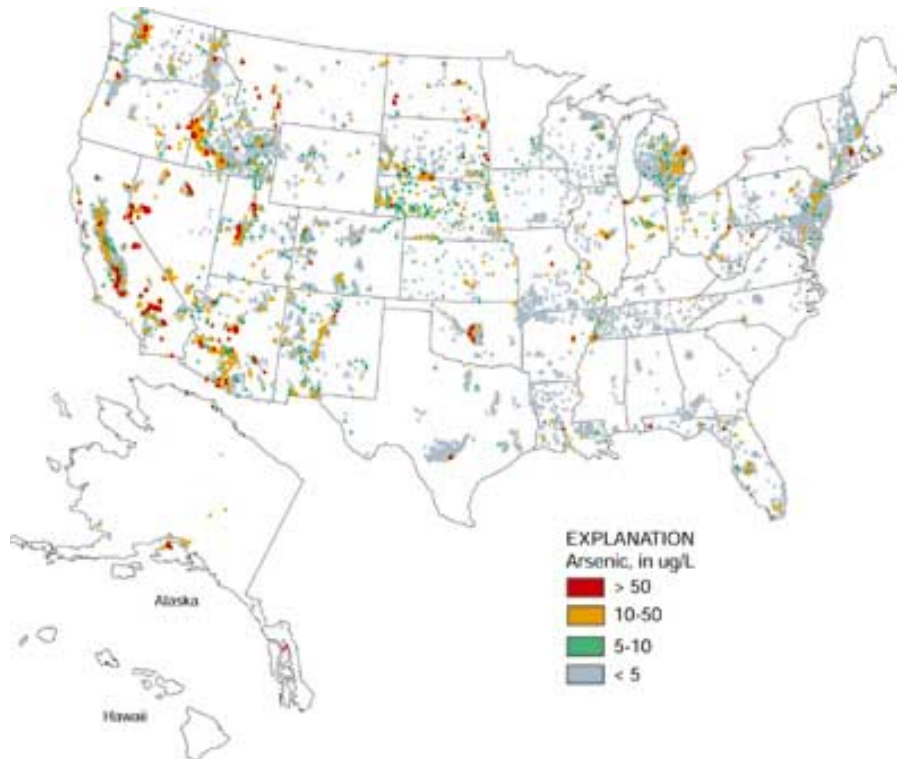


Table 1 below shows the estimated number of CWSs and NTNCWSs that would be affected by this rule and the estimated population served by these public water systems.

Table 1. Estimates of the Number of CWSs and NTNCWSs That Would Need to Treat and the Population Served by These Systems

Regulatory Action	Type of System and Total Number	Number Systems Affected	Total Population Served by the Affected System
10 µg/L	CWSs (54,000)	~ 3,000	~ 11 million
10 µg/L	NTNCWSs (20,000)	~ 1,100	~ 1.7 million

8. How much will this rule cost?

The EPA estimates the total national annualized costs of treatment, monitoring, reporting, recordkeeping, and administration for this rule to be approximately \$181 million (using 1999 dollars at a three percent discount rate - Table 2). Most of the cost is due to the cost of installing and operating the treatment technologies needed to reduce arsenic in public water systems (both CWSs and NTNCWS). The EPA estimates the total treatment cost to be approximately \$177 million per year. Annual monitoring and administrative costs will be about \$2.7 million and States' costs will be approximately \$1 million.

August 2002 Arsenic Guidance Appendix N-10

Table 2. Annual National System and State Compliance Costs (3% Discount Rate, \$millions)

	CWS	NTNCWS	Total
System Costs			
Treatment	\$170	\$7.0	\$177
Monitoring/Administrative	\$1.8	\$0.9	\$2.7
State Costs	\$0.9	\$0.1	\$1.0
Total Cost	\$173	\$8.0	\$181

The average annual household costs for the homes served by the approximately 2,387 CWSs that require treatment are expected to be approximately \$32 per year. The average annual household costs are shown categorized by system size in Table 3. The disparity in household costs between system size is due to economies of scale. Larger systems are able to spread the costs they incur over a larger customer base.

Table 3. Total Annual Costs (Dollars) per Household for CWSs

System Size	25-500	501-3,300	3.3K-10K	10K-and above
Annual	\$ 327-\$162	\$ 71-\$58	\$ 38	\$32-\$0.86

Household Costs

The estimated average annual costs for CWSs, which exceed the final MCL of 10 µg/L and are required to treat, are shown in Table 4 categorized by system size.

Table 4: Average Annual Costs per CWS (Dollars)

CWS System Size	Costs (\$)
25-500	\$6,494-\$12,358
501-3,300	\$22,100-\$53,086
3,300-10,000	\$111,646
10,000 and above	\$531,584-\$1,340,716

What are the Benefits of this Rule?

The rule will protect approximately 13 million Americans served by CWSs and NTNCWSs (this number is based on reducing arsenic from 50 to 10 µg/L). Reducing arsenic from 50 to 10 µg/L will prevent ~ 19-31 cases of bladder cancer and ~ 5-8 deaths due to bladder cancer per year.

The EPA estimates that reducing arsenic from 50 to 10 µg/L will prevent ~ 19-25 cases of lung cancer and ~ 16-22 deaths due to lung cancer per year. In addition to these quantified benefits, there are substantial non-quantified benefits of this rule, including reducing the incidences of non-cancerous effects summarized above.

The quantified annual benefits for the today's rule range from \$140 to \$198 million. The benefit range consists of both lower and upper bound estimates. These estimates reflect the upper and lower bound of the risk range addressed by this rule as well as different drinking water consumption distributions that were used in our analysis.

Is there funding associated with this rule?

Since 1996, the DWSRF has made over \$3.2 billion available for loans to help water systems improve their infrastructure. The EPA also provides funding to States that have primary enforcement responsibility for their drinking water programs through the Public Water Systems Supervision (**PWSS**) grants program. Other federal funds are available through Housing and Urban Development's Community Development Block Grant Program, and the Rural Utilities Service of the U.S. Department of Agriculture. In the most recent year, 2000, the DWSRF and Rural Utilities Service combined made \$1.7 billion available to States and public water systems for capital improvements and infrastructure needs.

How did EPA consult with stakeholders?

From 1997-1999, the EPA conducted a number of Agency workgroup meetings on arsenic as well as five stakeholder meetings across the country. Representatives of eight federal agencies, 19 State offices, 16 associations, 13 corporations, 14 consulting engineering companies, two environmental organizations, three members of the press, 37 public utilities and cities, four universities, and one Indian tribe attended the stakeholder meetings on arsenic.

Five States also provided written comments on implementation issues during the rule development process. The Office of Water staff presented an overview of the arsenic rulemaking to over 900 Tribal attendees in 1998 and provided more detailed information in 1999 to 25 Tribal council members and water utility operators from 12 Indian tribes.

As part of the Small Business Regulatory and Enforcement Flexibility Act (**SBREFA**) consultation process, the EPA also received substantial input from discussions with small entity representatives. The National Drinking Water Advisory Council (**NDWAC**) provided useful input, particularly on the benefits analysis and small systems affordability.

The EPA also posted discussion papers produced for our stakeholder interactions on the Office of Ground Water and Drinking Water (**OGWDW**) Internet site and sent them directly to participants at stakeholder meetings and others who expressed interest.

In addition, the EPA provided updates on rulemaking activities at national and regional meetings of various groups and trade associations.

Furthermore, the EPA participated in technical workgroup meetings held by the American Water Works Association (AWWA). The EPA received comments from over 1,100 commenters from the public on the proposed rule. The EPA has considered these comments carefully in developing today's final rule for arsenic.

Where can the public get more information about this final rule?

For general information on arsenic in drinking water, contact the Safe Drinking Water Hotline, at (800) 426-4791, or visit the EPA Safewater website at <http://www.epa.gov/safewater> or the arsenic website at <http://www.epa.gov/safewater/arsenic.html>.

In addition to this technical fact sheet, the following documents and fact sheets will be available to the public at the EPA's web site on arsenic in drinking water:

- Federal Register notice of the final arsenic regulation
- Detailed technical support documents on Arsenic in Drinking Water
- Consumer Fact Sheet on Arsenic in Drinking Water

A copy of the Federal Register notice of the final regulation or any of the technical and consumer facts sheets can be obtained by contacting the Safe Drinking Water Hotline at (800) 426-4791 and (703) 285-1093. The Safe Drinking Water Hotline is open Monday through Friday, excluding federal holidays, from 9:00 a.m. to 5:30 p.m. Eastern Time.



Lesion caused by high level of Arsenic in the drinking water.

Arsenic Sources

There are many small abandoned mines in the US which produce acid mine drainage effluent which contains up to 20ppm of arsenic and many heavy metals such as copper and zinc. This one on the right is in Montana.



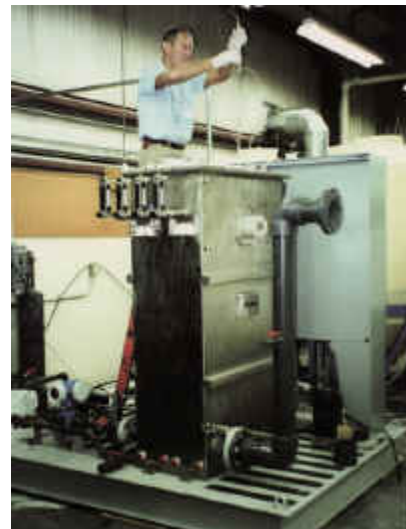
The dissolved iron which occurs naturally in acid mine drainage streams will be activated by sunlight so that it can catalyze the oxidation of both arsenic and iron.



Alternatively, a commercially manufactured UV lamp reactor can be used to achieve faster oxidation of acid mine water and for the stabilization of flue dust. These demonstrations were conducted with MSE and funded by the USEPA.

Patent 2 Sulfite and Short Wavelength Ultraviolet light

Drinking Water Treatment in Small WTP for Rural Townships



This 10 gpm reactor is used to demonstrate the oxidation of arsenic in a small town's water supply in Northern California. After oxidation, the arsenic was removed with iron hydroxide to produce clean water which contained less arsenic than the new stringent health limits.



Applications in Bangladesh

Patent 1 Iron and Sunlight or UV light

Families across Bangladesh rely on hand dug water for drinking. The tubewell of this family, like many others (50-70 million people), has been painted red signifying that the water naturally contains a dangerous amount of arsenic. Many thousands of villagers who have drunk the water for several years have developed skin cancers from the water.



AusAID has funded a demonstration Project in Bangladesh. The first step of the process involves dissolving a few grams of iron salt into forty liters of tubewell water and leaving it exposed to sunlight for a few hours.



After solar oxidation the arsenic contaminated water is transferred into the CRC-ANSTO designed settling urn. After settling overnight the urn provides the convenience of 'clean drinking water on tap' to a Krishnapur villager.



No electricity is needed for this low-tech process which is planned for use in rural areas of Bangladesh.

Analysis in remote locations

The Australian Nuclear Science and Technology Organization (**ANSTO**) team has overcome many difficulties to be able to determine trace arsenic concentrations immediately at our field sites.



Solid Waste Stabilization

Iron hydroxide is the most effective adsorbent for arsenic known. However, it is very difficult to dewater and normally dries to be very dusty. The chunky solid in this photo was produced by carefully controlling the drying conditions. Further stability can be attained by incorporating the solid in cement.

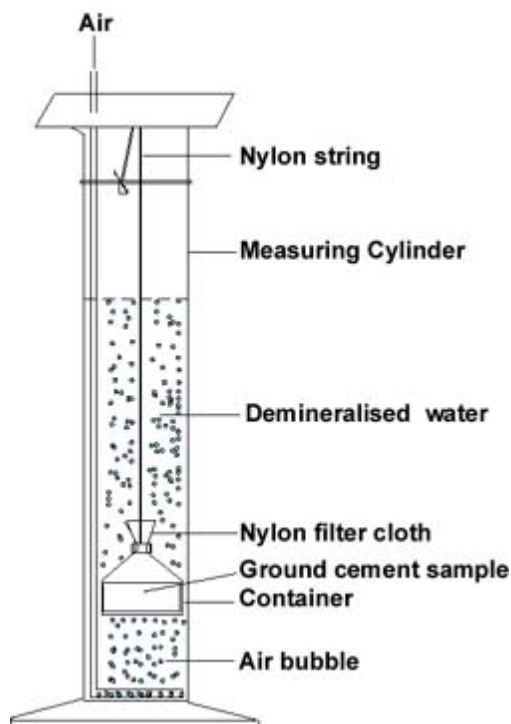


The water treatment residues, with and without cement encapsulation, passed the standard US EPA TCLP leach test for landfill disposal.



Leachability Testing

ANSTO routinely conduct the regulatory leaching tests including the TCLP. When arsenic wastes are not properly stabilized they are prone to reaction with atmospheric carbon dioxide. In order to identify problem solids ANSTO has developed a simple long-term leach test in aerated water.



The ANSTO group has been working in this varied field of arsenic remediation and advanced oxidation technologies for a decade and welcomes new challenges.

ANSTO Environment

ANSTO Environment is the largest multidisciplinary environmental research organization in Australia and the largest research unit at ANSTO. Australian Nuclear Science and Technology Organization (**ANSTO**)

For more information contact:

Tae Passfield
ANSTO Environment (Bld 21a)
ANSTO
PMB 1 Menai, NSW 2234

Patent 1

Khoe G.H., Emmett M.T. and Robins R.G.(1997)'Photo assisted oxidation of species in solution'. US Patent No. 5,688,378. Emmett, M and Khoe, G. (2001) Photochemical oxidation of arsenic by oxygen and iron in acidic solutions. Water Research, 35, 649-656

Patent 2

Khoe, G. H., Zaw, M. Prasad, P. S. and Emmett, M. T. (1999) Photo-assisted oxidation of inorganic species in aqueous solutions, International Patent Number: WO 99/05065, International Publication date: 4 February 1999.

Exemptions & the Arsenic Rule

The EPA's goal was to have all water systems comply with the 10 ppb arsenic maximum contaminant level (**MCL**) by January 23, 2006. The EPA understood, however, that additional time may be necessary for some systems to comply with the revised MCL, and believed that exemptions under §1416 of the Safe Drinking Water Act (**SDWA**) were an appropriate mechanism to provide this additional time.

Exemptions can help ensure that systems which are unable to comply with the revised arsenic MCL will have the opportunity to gain the resources or take the steps needed to comply with the rule in an appropriate period of time. The use of exemptions will also allow systems time to develop a plan for long-term capacity. States can act before the revised arsenic MCL goes into effect and move water systems more expeditiously toward compliance.

All public water systems (**PWSs**) that meet the minimum criteria outlined in the SDWA are eligible for an exemption of up to three years. For smaller water systems, exemptions can provide up to nine additional years beyond the compliance date of the MCL to achieve compliance. The EPA anticipates that States will grant systems only as much additional time as is needed to build capacity and come into compliance.

Without exemptions, water systems might not begin to move toward compliance until 2006. Exemptions encourage water systems to start down the path to compliance now, so that public health is better protected.

Exemptions are administrative tools that States can use in their long-term strategies to build capacity in drinking water systems. The use of exemptions gives eligible systems additional time to build capacity in order to achieve and maintain regulatory compliance, while continuing to provide acceptable levels of public health protection.

States can use exemptions during the implementation of the Arsenic Rule. The use of exemptions helped ensure that systems which were unable to comply with the arsenic MCL by January 23, 2006 would have the opportunity to gain the resources needed to comply with the rule in an appropriate period of time.

The EPA encourages the use of exemptions as a means of providing additional time to eligible systems. There are a number of criteria which systems must meet to be eligible for an exemption. First, the State have adopted the August 14, 1998 Variance and Exemptions Regulation (63 FR 43835).

Since some States may choose not to allow exemptions, systems under their jurisdiction will not be able to obtain an exemption. For States with exemptions provisions, systems must meet certain eligibility criteria as outlined in SDWA §1416. Systems that meet these eligibility requirements may qualify for different exemption durations depending on system size, arsenic concentrations, system needs, and other State requirements, if any.

Finally, the State must provide notice and opportunity for a public hearing. If the exemption is approved, the State must prescribe a compliance schedule. This document shows how exemptions can be granted in a straightforward and streamlined manner. It is divided into 2 sections.

Section 1 explains in a question and answer (Q&A) format how the applicable laws and regulations can be translated into a workable set of exemption guidelines. Section 2 is a “**How To**” guide demonstrating how straightforward the granting of an exemption can be.

Section 2 also includes two forms that can simplify the exemption process. The first form is for systems to use when requesting an exemption. The second form is for States to use when determining whether to grant an exemption. Both forms are accompanied by line-by-line instructions that explain the information needed and the types of paperwork necessary to document an exemption.

SECTION 1: EXEMPTION Q&A

1. What is an exemption?

Exemptions are administrative tools that allow water systems additional time to acquire financial assistance and develop mechanisms necessary to ensure compliance with a drinking water standard.

PWSs were required to meet the revised arsenic MCL of 10 ppb by January 23, 2006 (40 CFR 141.6(j)). To avoid noncompliance, exemptions had to be issued prior to this date. If granted an exemption, a PWS would have up to 3 additional years to comply (January 23, 2009). Eligible systems serving fewer than 3,300 persons may be granted up to 3 exemption extensions of 2 years each (SDWA §1416(b)(2) and 40 CFR 142.20(b)(2)), allowing up to 9 total years (14 years since the rule was published) to obtain financial assistance and implement a compliance strategy (January 23, 2015).

This Q & A document explains what States need to consider in granting exemptions and suggests a simple, straightforward, and effective manner in which States can document their decisions regarding exemptions.

2. Which systems are eligible for exemptions?

A system is eligible for an exemption from the arsenic MCL if, at a minimum, it meets all four of the following criteria (40 CFR 142.20(b) and SDWA §1416(a)):

1. “Due to **compelling factors**,” (40 CFR 142.50) the PWS is unable to achieve compliance by January 23, 2006 through any means, including treatment or developing an alternative source of water supply.
2. The PWS “**was in operation**” by January 23, 2006 or, if not in operation by January 23, 2006, the system has “no reasonable alternative source of drinking water” available to it.
3. The exemption “**will not result in an unreasonable risk to health.**”
4. The system cannot reasonably make **management and/or restructuring changes** that would result in compliance or improve the quality of the drinking water if compliance cannot be achieved. Section 2 provides a simple form that States can use to document system eligibility for an exemption and, if appropriate, the findings and conditions associated with granting an exemption.

3. How can a system indicate its interest in receiving an exemption?

Section 2 also provides a simple form that systems can use to request an exemption, if allowed by the State. States that choose to use the exemption provision can modify the form to fit their needs. Systems that need exemptions will generally have limited technical, financial, and managerial capacity. Therefore, States and technical assistance

providers may want to make a special effort to alert systems to the potential availability of exemptions and to assist them in completing an application.

4. Under what minimum conditions may an eligible system receive an exemption from the arsenic MCL?

To receive an exemption from its State, an eligible PWS must, at a minimum, be “**taking all practicable steps to meet**” the MCL (40 CFR 142.20(b), 40 CFR 142.50(b), and SDWA §1416(b)(2)(B)). In addition, no exemption shall be granted by a State unless the PWS establishes that:

1. In order to meet the MCL, the system needed capital improvements that could not be completed prior to January 23, 2006;
2. In the case of a system that needs financial assistance for the necessary improvements, the system has entered into an agreement to receive the necessary financial assistance or has demonstrated that such financial assistance, either from a federal or State program, is “**reasonably likely to be available within the period of the exemption**”; or,
3. The system has entered into an enforceable agreement to become part of a regional water system (SDWA §1416(b)(2)(B)).

For example, a PWS that needs capital improvements and requires financial assistance could provide written documentation showing its position on the Drinking Water State Revolving Fund (**DWSRF**) priority list. Alternatively, the PWS could document its loan agreement with a private lender, or provide a written and enforceable agreement to become a part of a regional PWS.

When reviewing a system’s need for capital improvements that could not be completed prior to January 23, 2006, the State had to determine whether it was feasible for the system to design an appropriate treatment train, obtained sufficient funding, and installed the treatment technology by January 23, 2006. Systems should consider installing a Best Available Technology (**BAT**), and small systems should consider installing a small system compliance technology (**SSCT**) listed in the Final Arsenic Rule (40 CFR 141.62(c) & (d)).

Systems and states should consider the possibility of upgrading the system’s existing treatment capabilities and the installation of additional treatment technology. If modification or installation before January 23, 2006 was not feasible due to compelling circumstances, the system might be eligible for an exemption.

In addition, the state had to consider whether the system could develop or gain access to an alternative water source by January 23, 2006 [40 CFR 142.20(b) and 40 CFR 142.50(a)]. The feasibility of establishing a partnership to use a neighboring system’s source must be considered along with the development of a new source [40 CFR 142.20(b)(1)(ii)]. PWSs and states should consider whether the characteristics of the new source would require the system to treat for other contaminants and, consequently, make using the new source cost prohibitive.

If, due to compelling reasons, the system cannot implement measures to develop an alternative source before January 23, 2006, the system was eligible for an exemption.

1For additional details, see Question 10.

5. Under what minimum conditions may an eligible system qualify for an exemption extension?

PWSs that receive exemptions and serve no more than 3,300 persons may be able to extend their exemptions by up to 6 years. These extensions can be considered and granted when the State grants the original 3-year exemption.¹ These extensions provide States the flexibility to develop compliance schedules longer than 3 years. A system is eligible to extend its exemption only if, at a minimum, it:

1. Proves that it is taking all practicable steps to meet the established schedule to achieve full compliance with the arsenic MCL.
2. Needs financial assistance for the necessary improvements and has entered into an agreement for, or is reasonably likely to obtain (from a federal or State program), financial assistance to make necessary capital improvements, or has entered into an enforceable agreement to become a part of a regional public water system (40 CFR 142.20(b) and SDWA §1416(b)(2)(C)).

States may grant up to three additional 2-year extensions during which systems are exempt from the MCL. The extensions should be based on how much time the system reasonably needs to come into compliance. A primacy State must document its findings when extending an exemption (40 CFR 142.20(b)(2)). Again, these findings can be based on easily acquired or readily available information and can be documented in a streamlined and straightforward manner.

EXEMPTION ELIGIBILITY ISSUES

6. What are “compelling factors”?

As a minimum condition for receiving an exemption, a system had to be unable to achieve compliance by January 23, 2006, due to compelling factors [40 CFR 142.20(b), 40 CFR 142.50(a)(1), and SDWA section 1416(a)(1)].

According to the SDWA, compelling factors may include economic factors, including qualification of the PWS as a system serving a disadvantaged community pursuant to SDWA section 1452(d). SDWA section 1452(d) defines a disadvantaged community as “the service area of a PWS that meets affordability criteria established after public review and comment by the State in which the public water system is located.” Among the factors a State may wish to consider in determining whether a system needs additional time to achieve compliance are the following:

1. The number and types of activities that should reasonably be undertaken, consistent with the size of the system and the financial consequences to its ratepayers, in order to choose and implement an appropriate technology. These activities may include pilot-testing or field-testing arsenic-removal technologies, selecting an engineering consultant, coordinating with State and local agencies, preparing plans and specifications, obtaining financing, obtaining bids for construction, obtaining permits, constructing the facilities, and testing the completed facilities.
2. The time appropriately allocated for each of the activities identified in (1), and the total time allocated for all activities.
3. The cost of performing the activities identified in (1), and any savings that might be obtained from additional time.
4. The benefits that may be obtained from additional time, including any improvements in cost-effectiveness that may be obtained from non-BAT technologies or from ascertaining which technology may be most appropriate for the raw water supplies available to the system.

Other compelling factors affecting a system's ability to comply may be identified by the state on a case by-case basis. The EPA recognized many systems may have difficulty in achieving compliance by January 23, 2006. There was a wide variety of circumstances the states would have to consider, and there might be sufficient variation so that "**compelling circumstances**" could not be strictly defined.

7. How can a PWS beginning operation after January 23, 2006 qualify for an exemption?

At a minimum, a PWS that begins operation after January 23, 2006 must show that it has "**no reasonable alternative source of drinking water**" in order to qualify for an exemption (40 CFR 142.20(b) and SDWA §1416(a)(2)). Such a system should show that it is not feasible to develop an alternative source of water which has a lower level of arsenic or to access a neighboring system's water source. A system that successfully demonstrates it has no reasonable alternative source of drinking water may be eligible for an exemption. To be eligible, new systems still must meet all other exemption eligibility criteria that apply, including:

1. The presence of a compelling factor which prohibits the system from complying by January 23, 2006.
2. The absence of unreasonable risk to health.
3. The lack of available management or restructuring changes that would result in compliance or, if compliance cannot be achieved, would improve water quality.

8. What constitutes an "Unreasonable Risk to Health"?

An exemption from the revised arsenic MCL requires, among other things, that the exemption will not result in an unreasonable risk to health. An exemption to an MCL allows a PWS to continue to provide water at some level above the MCL for a specified period of time, after which the system must come into compliance.

In this guidance, the EPA is suggesting an approach to determine what does **not** constitute an unreasonable risk to health with respect to arsenic. This approach bases the length of an exemption on the level of arsenic in the water. States may use an alternate method to the following approach.

The EPA's approach is based on the fact that Congress included exemption provisions in the SDWA with the clear intention that they be used to address the needs of economically challenged systems by providing additional time to achieve compliance. Congress necessarily contemplated that the customers of these systems would be exposed to drinking water above the MCL for the period of the exemption.

The limitation that Congress imposed on this excess exposure is that it not constitute an unreasonable risk to health. The EPA is suggesting one possible approach to determining what does not pose an unreasonable risk to health with respect to arsenic, rather than addressing the much more complex issue of what **does** constitute an unreasonable risk to health.

In reauthorizing the SDWA, Congress established a time frame for implementation that allows systems up to 5 years to comply with new or revised regulatory requirements. Under the revised MCL of 10 ppb, water systems are allowed to continue to operate at levels between 10 ppb and 50 ppb for up to 5 years.

Through the time frame allowed in SDWA, Congress made the tacit determination that these exposures will pose an acceptable, and therefore not “**unreasonable**” risk of adverse health effects to the affected population. Based on that determination and on information suggesting a linear relationship between the arsenic dose and cancer risk, the EPA is suggesting concentration levels that should not generally pose an unreasonable risk to health for exemptions of various durations.

The previous arsenic MCL was 50 ppb. Systems had to begin complying with the revised MCL of 10 ppb by January 23, 2006, five years from the date the Arsenic Rule was published (January 22, 2001). Thus, in principle, a system could be providing water with an arsenic level of 50 ppb until January 23, 2006 and be in full compliance with the SDWA and EPA regulations. The system would remain in compliance if it reduced its arsenic level to 10 ppb or less by January 23, 2006.

Exemptions could extend the compliance date by up to 3 years or up to 9 years, depending on system size and number of extensions granted. The longest period a system could have to achieve compliance would be 14 years (the 5-year base of January 22, 2001-January 23, 2006, plus a 3-year exemption and three 2-year extensions). As a matter of congressional policy, exposure at 50 ppb for the 5 years from January 22, 2001 to January 23, 2006 should **not** pose an unreasonable risk to health. This represents 40 ppb above the revised MCL of 10 ppb (50 ppb-10 ppb = 40 ppb).

The total exposure above the revised MCL for those 5 years is $40 \text{ ppb} \times 5 \text{ years} = 200 \text{ ppb} \times \text{years}$.

This $200 \text{ ppb} \times \text{years}$ may be thought of as the “**excess compliance-period exposure.**” That is, it represents the exposure above what would have occurred if water systems had instantaneously complied with the revised MCL on January 22, 2001. It represents “**excess exposure**” that, as a matter of law and policy, should not pose an unreasonable risk to health.

The EPA’s policy is to assume a linear relationship between adverse health effects of a chemical and exposure unless there are sufficient data to decide otherwise. In its review of the Arsenic Rule extending into fall 2001, the scientific community again endorsed the EPA’s decision to use a linear approach for estimating arsenic risks.

Exemptions and any subsequent extensions cannot be granted for more than 9 years and for concentrations higher than 50 ppb. Thus, for an exemption, the determination of what concentration level and duration does not pose an unreasonable risk to health can be conservatively determined by limiting “**excess compliance-period exposure**” to $\#200\text{ppb} \times \text{years}$ for the total compliance period including the full duration of an exemption.

The following calculations clarify the application of this concept:

$(5 \text{ years}) \times (40 \text{ ppb}) = 200 \text{ ppb} \times \text{years}$

$(8 \text{ years}) \times (C8) = 200 \text{ ppb} \times \text{years}; (C8) = (200\text{ppb} \times \text{years})/(8 \text{ years}) = 25 \text{ ppb}$

Thus, for an initial 3-year exemption (which provides a total compliance period of 8 years), a concentration of 25 ppb above the MCL of 10 ppb (a total concentration of 35 ppb) would not generally pose an unreasonable risk to health.

$(10 \text{ years}) \times (C_{10}) = 200 \text{ ppb} \times \text{years}$; $(C_{10}) = (200 \text{ ppb} \times \text{years}) / (10 \text{ years}) = 20 \text{ ppb}$
 Thus, for a 2-year extension to the initial 3-year exemption (which provides a total compliance period of 10 years), a concentration of 20 ppb above the MCL of 10 ppb (a total concentration of 30 ppb) would not generally pose an unreasonable risk to health.

$(12 \text{ years}) \times (C_{12}) = 200 \text{ ppb} \times \text{years}$; $(C_{12}) = (200 \text{ ppb} \times \text{years}) / (12 \text{ years}) = 17 \text{ ppb}$
 Thus, for two 2-year extensions to the initial 3-year exemption (which provides a total compliance period of 12 years), a concentration of 17 ppb above the MCL of 10 ppb (or a total concentration of 27 ppb) would not generally pose an unreasonable risk to health.

$(14 \text{ years}) \times (C_{14}) = 200 \text{ ppb} \times \text{years}$; $(C_{14}) = (200 \text{ ppb} \times \text{years}) / (14 \text{ years}) = 14 \text{ ppb}$
 Thus, for three 2-year extensions to the initial 3-year exemption (which provides a total compliance period of 14 years), a concentration of 14 ppb above the MCL of 10 ppb (or a total concentration of 24 ppb) would not generally pose an unreasonable risk to health.

Based on these calculations, the EPA believes the values in Table 1 offer a conservative and appropriate framework for determining the duration of an exemption that should not generally pose an unreasonable risk to health for systems with various historical arsenic concentrations. As a result, States may wish to consider exemptions for the indicated arsenic concentrations over the indicated time periods.

Table 1: Exemption Eligibility Based on “Unreasonable Risk to Health” Criteria

Table 1: Exemption Eligibility Based on “Unreasonable Risk to Health” Criteria

Systems Serving	Total Compliance Time after 01/22/2001	Exemption Periods Available	Would an exemption be granted for these arsenic concentrations?				
			> 35 ppb	> 30 ppb but < 35 ppb	> 25 ppb but < 30 ppb	>20 ppb but < 25 ppb	≤ 20 ppb
> 3,300 persons	8 years	3 years (2006-2009)	No	Yes	Yes	Yes	Yes
≤ 3,300 persons	8 years	3 years (2006-2009)	No	Yes	Yes	Yes	Yes
	10 years	5 years (2006-2011) ^a	No	No	Yes	Yes	Yes
	12 years	7 years (2006-2013) ^b	No	No	No	Yes	Yes
	14 years	9 years (2006-2015) ^c	No	No	No	No	Yes

a Includes the initial 3-year exemption available to all systems and the first of three 2-year small system extensions.

b Includes the initial 3-year exemption available to all systems and two of three 2-year small system extensions.

c Includes the initial 3-year exemption available to all systems and all three 2-year small system extensions.

Note that, in determining the arsenic concentrations allowable in small systems that receive the second and third extensions available to them, the EPA suggests that States round down the allowable concentrations relative to the values shown in the calculations discussed above.

This rounding down provides an additional margin of safety, given the relatively long durations of elevated exposures that would be experienced by the individuals served by these systems.

This analysis is predicated on the assumption that a system will seek an exemption based on the historical concentration of arsenic in its source water. In other words, under this approach exemptions would not be available for systems that historically have had arsenic concentrations above 35 ppb, even if those systems have recently taken steps to reduce their concentrations to 35 ppb or less.

Furthermore, under this approach, exemptions would not offer a stair-step path to compliance. Systems could not obtain a 3-year exemption with a concentration of 35 ppb, and then seek an extension to that exemption by blending or otherwise reducing their concentrations to 30 ppb. Under this approach, the total length of the exemption for which a system is eligible is determined by the historical concentration of arsenic in the system's source water at the time of application for an exemption.

9. What did the state have to consider concluding that management or restructuring changes could not reasonably be made to achieve compliance or improve the drinking water quality by January 23, 2006?

The regulation [40 CFR 142.20(b)(1)] defines the measures a state must consider before determining that management or restructuring changes cannot reasonably be made by a system to achieve compliance or, if compliance cannot be achieved, improve the quality of its drinking water. This task need not be onerous or time consuming.

Rather, the state can use information from existing files, site visits, and telephone conversations with system managers to make determinations, and can quickly and briefly document such determinations.

The state determination form in Section 2 is an example of such streamlined documentation.

In making the determination, the State must consider what a system could reasonably accomplish through all of the following (40 CFR 142.20(b)(1)(i)):

1. Rate increases.
2. Accounting changes.
3. Appointment of a state-certified operator (under the State's Operator Certification program).
4. Joint operation with one or more PWSs (through a contractual agreement).
5. Activities consistent with the State's Capacity Development Strategy (to help the PWS acquire and maintain technical, financial, and managerial capacity).
6. Ownership changes.
7. "Consolidation (physical or otherwise) with another PWS."

In addition, the state must consider whether the DWSRF or other forms of federal or state assistance are "***reasonably likely to be available within the period of the exemption***" to implement the appropriate measures [40 CFR 142.20(b)(1)(i)]. If none of these measures was feasible by January 23, 2006, the system might be eligible for an exemption if the other three criteria listed above in the answer to Question 2 are met.

A state had to document its findings when determining that appropriate management or restructuring changes could not reasonably be made by January 23, 2006 [40 CFR 142.20(b)(1)]. Such documentation may conveniently be prepared using a form such as that suggested in Section 2.

²Excludes EPA Regions responsible for direct implementation.

GRANTING AND EXEMPTION

10. What must States document in granting an exemption to a system?

When a state grants an exemption to a PWS, it “**must document all findings required under SDWA section 1416**,” including management and restructuring changes (40 CFR 142.20(b)(1)). States must document financial assistance needs when granting an extension (40 CFR 142.20(b)(2)).

States must provide the reasons for granting each exemption, including documenting the need for the exemption and providing the reason that the exemption will not result in unreasonable risk to health (40 CFR 142.15(a)(3)). The documentation process does not need to be onerous or time consuming. The State determination form in Section 2 suggests a streamlined approach to State documentation.

11. What else is expected from States during the exemption process?

The EPA encourages States to have systems request an exemption as soon as possible after determining that January 2006 compliance is not feasible. By beginning the exemption process early, States and systems have more time to conduct public hearings, identify the solutions necessary to bring systems into compliance, and set compliance schedules.

A State must decide whether to grant an exemption within 90 days (or less as prescribed by State rules) of receiving the exemption request (40 CFR 142.21 and 40 CFR 142.52).

The State should use the information it has about the system, as well as supplementary information provided by the system, to determine whether the system is eligible.

States will have to exercise their discretion in granting exemptions. The EPA will review the decisions made by a primacy State in accordance with 40 CFR 142 Subpart C (which provides that the EPA will review a State’s exemptions to determine whether the State has abused its discretion or failed to establish a compliance schedule as required by SDWA §1416(b)(1)).

Section 2 offers an example of an “**Exemption Request Form**” for systems seeking an exemption. The EPA suggests that States and technical assistance providers work with systems most likely to need exemptions to help them complete such a form.

When a State grants an exemption, it must at the same time set a compliance schedule for the system, including increments of progress, or milestones (40 CFR 142.20(b), 40 CFR 142.53, and SDWA §1416(b)(1)). The schedule should require compliance as “**expeditiously as practicable**” (SDWA §1416(b)(2)(A)).

In addition, the State must prescribe a schedule for the system to implement control measures for arsenic during the period of the exemption (40 CFR 142.20(b), 40 CFR 142.53(c) and SDWA §1416(b)(1)). Before the schedules for compliance and control measures take effect, the State must notify and give the public an opportunity to comment on the schedules (40 CFR 142.20(b), 40 CFR 142.54, and SDWA §1416(b)(1)).

Public participation is a key component of the new flexibilities (i.e., exemptions) to SDWA, allowing impacted consumers to participate in making key decisions. None of these tasks need be overly burdensome. For example, States can hold joint hearings on groups of exemptions within a geographic area to minimize the administrative burden without compromising consumer participation.

Other efficiencies can be developed by States to streamline the process and make exemptions a viable and effective option for ensuring long-term compliance.

During the deliberation process, the State can also determine whether an extension will be necessary for an otherwise eligible system to implement its compliance strategy (including securing financial assistance).

“The Agency interprets the extension provisions for public water systems serving less than 3,300 persons to allow the primacy agency to grant the additional two-year periods at the time of initial issuance of the exemption for those small systems that need financial assistance for the necessary improvements”
(63 FR 43843).

These extensions provide States the flexibility to develop feasible compliance schedules (i.e., longer than 3 years). In order to grant extensions beyond the initial exemption/extension period, the State must conduct a review to ensure that the system is taking all practicable steps to comply with the MCL and the exemption compliance schedule provided by the State (40 CFR 142.20(b)(2)).

If the State determines that a PWS is not taking all practicable steps to comply with the requirements, the exemption should not be extended. The PWS should be subject to enforcement to address violations of the established schedule and the Arsenic Rule requirements.

If the exemption is extended, the PWS should be in full compliance with the Arsenic Rule at the end of the extension period.

Below, summarizes the arsenic exemption process.

PWS determines it won't be able to comply with revised arsenic MCL by January 23, 2006 & requests an exemption from the State. State and PWS work together to determine if the system is eligible for an exemption and hold public hearing.

State informs PWS of exemption decision.

State sets a compliance schedule for the PWS (taking into account extensions) & appropriate control measures.

PWS implements compliance strategy, meeting all State milestones and informing customers as required.

State must decide whether to extend exemption (if applicable) by determining whether PWS is taking all practicable steps to stay on compliance schedule.

PWS continues to implement compliance strategy, meeting all State milestones and informing customers as directed.

PWS COMPLIES WITH MCL

PWS must comply with MCL by January 23, 2006.

Granted

Denied

PWS must comply with MCL.

Denied

Extended

DEADLINE

STATE MUST ACT WITHIN 90 DAYS AFTER REQUEST AS DETERMINED BY STATE

NO LATER THAN 1/23/09*

AS DETERMINED BY STATE

NO LATER THAN 1/23/15*

*Last feasible date. The EPA suggests taking action as early as possible.

12. What additional conditions may States impose on eligible systems for them to qualify for an exemption?

In addition to the compliance schedule, States may add conditions to the exemption to further reduce the health risk. For example, States may require systems to use bottled water, point-of-use devices, or point of entry devices as a condition of granting an exemption (40 CFR 142.57(a)). Under this condition, bottled water must meet the requirements in 40 CFR 142.62(g) and point-of-use or point-of-entry devices must meet the requirements in 40 CFR 142.62(h).

13. What should a system do once an exemption is granted?

When granted an exemption by its State, a PWS should follow the compliance schedule and meet all milestones. The system should understand how it will need to show progress and meet all other requirements of the exemption.

14. What are the system's reporting and public notification requirements?

In addition to the reporting and notification requirements outlined in the Arsenic Implementation Guidance Section I-A.7.d and I-A.7.e, systems operating under an exemption must include the following information in their consumer confidence report and public notice (40 CFR 141.153(g) and 40 CFR 141.205(b)):

1. An explanation of the reasons for the exemption.
2. The date on which the exemption was issued.
3. A brief status report on the steps the system is taking to install treatment, find alternative sources of water, or otherwise comply with the terms and schedules of the exemption.
4. A notice of any opportunity for public input in the review or extension of the exemption.

Systems operating under an exemption are required to issue a Tier 3 public notice and to notify their consumers within one year of receiving an exemption and repeat the notice annually for as long as the exemption applies to the system.

In addition, if the notice is posted, it must remain in place for as long as the exemption exists (40 CFR 141.204(b)(1)).

A system that violates the conditions of an exemption is required to issue a Tier 2 public notice (40 CFR 141.203(a)) containing the ten elements specified in 40 CFR 141.205(b).

HOW DO EXEMPTIONS FIT WITH OTHER PROGRAMS?

15. How can the DWSRF provisions and exemption provisions be used together?

Given the many competing demands placed on the DWSRF and other financial assistance programs, the flexibility to extend the period of time available for a system to receive financial assistance is important for States and systems. Exemptions help ensure that DWSRF assistance goes to PWSs most in need of such aid. Exemptions also allow systems that receive DWSRF assistance to be able to use it in a way that produces full compliance with an MCL.

The State must consider whether DWSRF assistance will likely be available within the time period of the exemption to implement necessary changes (40 CFR 142.20(b)(1)(i)). This requirement to consider the DWSRF as a possible funding source does not mean that the State must provide DWSRF assistance to a system seeking an exemption. States retain full authority to allocate SRF funds.

Another major source of federal financial assistance for water systems is the Rural Utility Service Water and Environmental Programs (**WEP**). WEP provides loans, grants, and loan guarantees for drinking water in rural areas and towns of up to 10,000 persons. Public bodies, non-profit organizations, and federally recognized Indian tribes are eligible for assistance.

Over \$1.5 billion in financial assistance was available from WEP in fiscal year 2001.

16. Can the variance and the exemption provisions be used together?

PWSs that receive a small system variance for arsenic are not eligible for exemptions (SDWA §1416(b)(2)(D)).

A State may grant a variance to a PWS after an exemption has been granted. Generally, this would be appropriate only if unforeseen changes in circumstances during the exemption period make compliance unaffordable for the system.

For instance, if a system installs a BAT during the exemption period, but still cannot comply with the MCL due to source water characteristics, the State may grant the system a general variance.

For more information, please refer to the document *Revision of Existing Variance and Exemption Regulations to Comply With Requirements of the Safe Drinking Water Act; Final Rule* (63 FR 43835 (August 14, 1998)).

OTHER TOOLS

17. How should States deal with systems that fail to meet the terms of their exemptions and come into compliance?

With appropriate State support and oversight, systems receiving exemptions should be able to achieve compliance by the time their exemptions expire. But in some States, systems may violate the terms of their exemptions or fail to be in compliance when their exemptions expire.

In such situations, States may wish to consider the use of Administrative Orders (AOs) to direct these systems to take positive steps toward compliance.

Often, States issue AOs to noncompliant systems after exhausting other administrative compliance options and instead of pursuing more formal civil or criminal relief.

Depending on the state authority, an AO may include, among other things, a finding of violation, a compliance schedule with milestones, and a provision for assessing stipulated penalties for any violation of the AO's terms. In most States, systems have the right to appeal the terms of the AO in the administrative arena (such as during an administrative hearing) or in the judicial system; depending upon State authority, a State may be able to commence contempt proceedings in a civil court, collection actions, receivership proceedings, or termination of service proceedings for violation of the AO's terms.

States can use an AO to describe the conditions under which the system would be allowed to continue to operate after the violation or expiration of the exemption, while acknowledging that the system is in violation of the revised MCL. The terms of the AO should ensure that the system is taking the steps needed to come into compliance in accordance with a State-prescribed schedule.

In addition to unilateral AOs, States may have the option of entering into Administrative Consent Orders (i.e., stipulated agreements) with noncompliant PWSs.

An Administrative Consent Order is a legal agreement between the State and the PWS in which the system agrees to pay for correction of violations and to take the required corrective action within an agreed-upon period of time.

Stipulated agreements generally have the same force and effect as AOs and are effective when a system wants to comply and has committed to a compliance schedule.

However, stipulated agreements, AOs, and other enforcement tools should not be viewed as alternatives to exemptions. Exemptions are the statutory tool of choice for helping eligible systems achieve compliance. Enforcement tools should be used only after non-compliance has occurred.

Congress explicitly created the exemption provisions to address the needs of systems facing difficult, "**compelling**" circumstances that preclude their being able to achieve compliance in the normal time frame. Exemptions can help systems from ever being in non-compliance.



TITRATION: Method of testing by adding a reagent of known strength to a water sample until a specific color change indicates the completion of the reaction.

HOW TO GRANT EXEMPTIONS

Granting an exemption can be simple and straightforward. For each exemption granted, it is important that the State work closely with the system to ensure that the exemption will result in compliance without jeopardizing the health of the system's customers. EPA encourages States to have systems request exemptions as soon as possible after determining that compliance is not feasible.

This gives States and systems more time to identify solutions and set appropriate compliance schedules to attain compliance as quickly as possible.

This Section provides two sample forms:

FORM #1: EXAMPLE SYSTEM REQUEST FORM. States can consider using this kind of form to collect important information from systems requesting exemptions.

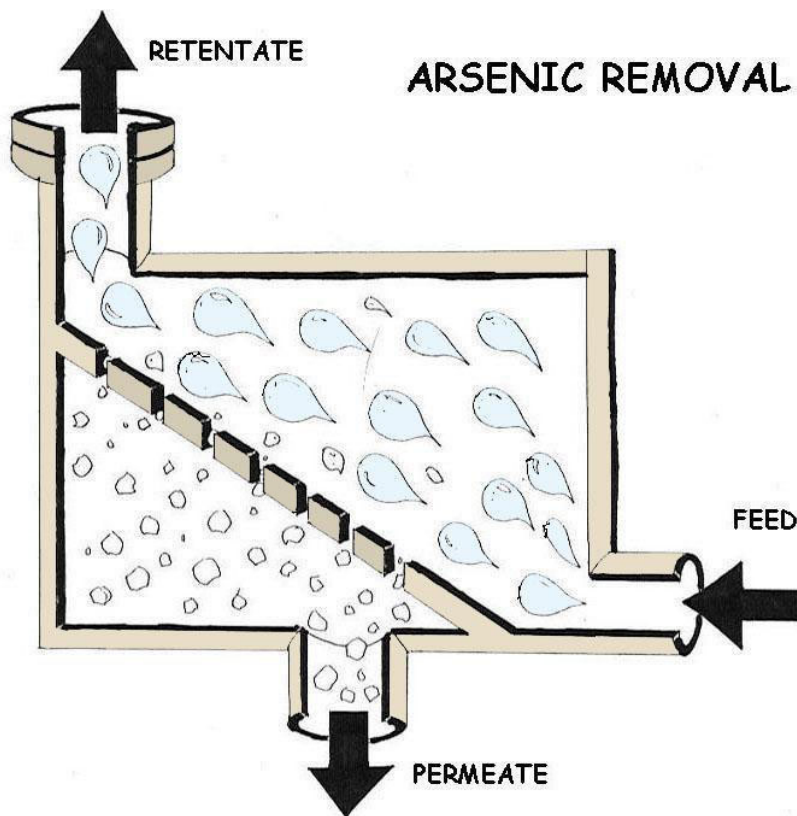
FORM #2: EXAMPLE STATE DETERMINATION FORM. States can consider using this kind of form to determine whether a system should be granted an exemption.

Each form is presented with step-by-step instructions. States should modify these forms to fit their needs.

States can use the **EXAMPLE SYSTEM REQUEST FORM** to gather information from each water system requesting an exemption. Systems needing exemptions will generally have limited technical, financial, and managerial capacity.

Therefore, States and technical assistance providers may wish to make a special effort to alert systems to the potential availability of exemptions and to assist them in completing applications such as the one discussed below.

States can use the **EXAMPLE STATE DETERMINATION FORM** to determine whether a system should be granted an exemption (and if necessary, an extension). The form allows the State to quickly document each eligibility assessment.



Is Your Ground Water System Installing Disinfection for Pathogen Control?

Water systems that disinfect their water should be aware of the possibility of an increase in arsenic concentrations in their distribution system, particularly if the water contains high concentrations of dissolved iron. When chlorinated, the dissolved iron forms particles on which arsenic can accumulate. As a result, high arsenic concentrations may occur in distribution system water even if arsenic concentrations in the raw water are below the MCL.

This happened to a small community water system in the Midwest that began chlorinating water from a series of wells that had raw water arsenic levels between 0.003 and 0.008 mg/L and iron concentrations up to 0.4 mg/L. At the same time, the system installed a polyphosphate feed system for corrosion control. Soon after chlorination began, the system received intermittent colored-water complaints from its customers with increasing frequency across the distribution system. Samples collected from several representative locations through out the service area had a reddish-brown color and contained particles. A metals analysis showed high levels of copper and iron oxides in the finished water, along with arsenic concentrations approaching 5 mg/L. Because of the water's colored appearance, it was considered unlikely that customers would consume the water. Doctors and health care professionals were notified of the situation and instructed to watch for signs of arsenic poisoning.

FORM #1: EXAMPLE SYSTEM REQUEST FORM PAGE 1 OF 2

- 1 System Name: 2 PWSID:
3 Contact Person: 4 Phone Number:
5 Address:
6 Date System Began Operating:
7 Have you received a variance for arsenic? YES NO
8 What is the range of arsenic levels in your finished water? High: Low:
9 Summarize your treatment process:
10 Arsenic treatment options considered:
11 Current water rate structure:
12 Does the system have a certified operator? YES NO
13 What steps have you taken to meet the MCL?
14 What capital improvements are needed?
15 Why can't these improvements be made before 1/23/06?
16 If financial assistance is needed, which of the following describes your system (include documentation):
• You have entered into an agreement to get the financial assistance
YES
NO
• You are reasonably likely to get financial assistance from a Federal or State source
YES
NO
17 Assistance Source: DWSRF RUS Other:

Date Applied: Contact:

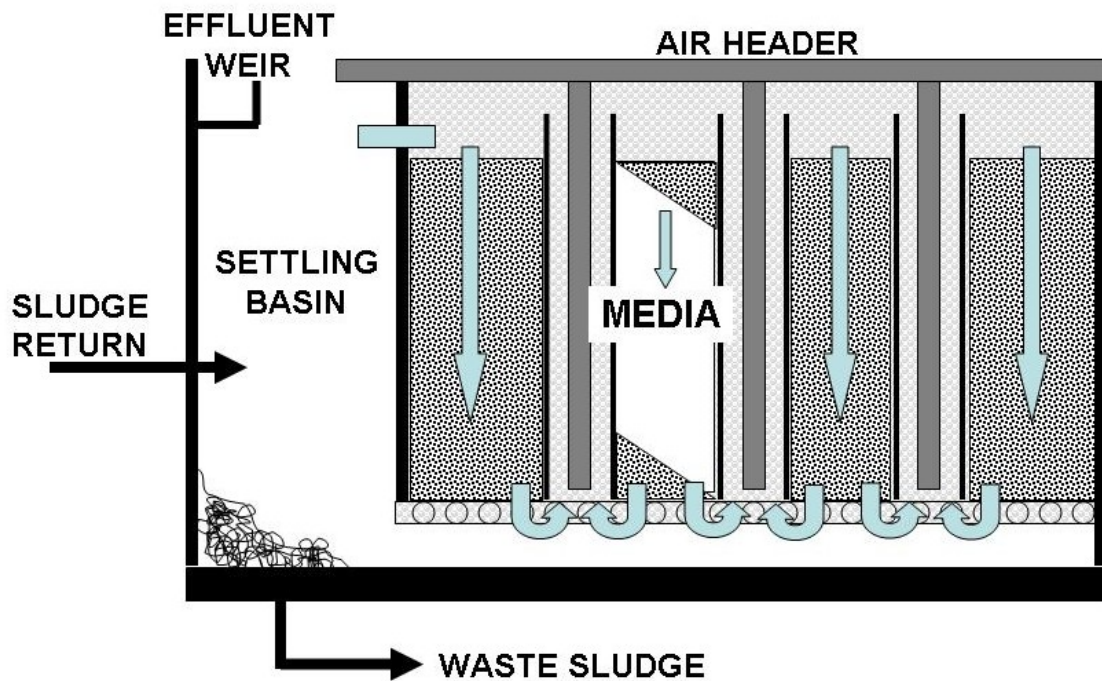
- 18 Have you entered into an enforceable agreement to become part of a regional PWS?
YES
NO
19 How much time do you need to:
• secure funding
• finish the capital improvement(s)
• begin operating in compliance with the revised MCL

Total time needed to come into compliance

20 If you will begin operation after 1/23/06, why can't your system use another source of drinking water with lower arsenic levels?

Submitted by: _____ Date: _____

Please use the space below to provide any other information that you would like the State to know when considering your request:
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Reducing pH During Treatment

Some arsenic treatment technologies require the pH to be reduced as a treatment step. If your system has adopted one of these techniques, be sure your pH is raised to a level that will not cause corrosion problems in your pipes. If you already have a corrosion control program in place, review whether you will need to adjust your corrosion chemical dose in response to any change in your water quality resulting from the installation of arsenic treatment. Keep in mind that adjusting the pH upward for lead and copper control may also cause arsenic to be released from scale on pipes and components.

System Request Form Instruction & Notes

Although the State should have system contact information on file, it is useful to have the most current information possible. This is particularly beneficial if someone besides the normal system contact is handling the exemption request.

Although the State will likely know when every system began operating, it is useful to verify this date. Systems that begin operations after January 23, 2002 must meet an additional eligibility requirement to receive an exemption.

Systems that have received a small system variance for arsenic are not eligible for an exemption. Currently, such variances cannot be granted.

Most systems should be able to provide a range of arsenic levels in their finished water from monitoring results for the current MCL. Systems that lack arsenic data should conduct sampling before applying for an exemption. The State will use these data to make its unreasonable risk to health determination.

The State can use the information about a system's treatment process and finished water arsenic levels to understand the treatment options available to a system. Using this information, the State may be able to suggest a low-cost strategy for modifying the treatment process or may determine that treatment modifications by January 23, 2006 are not feasible and affordable.

The State can use this information to ensure that systems have considered all reasonable arsenic compliance options. The State may be able to suggest strategies the system did not consider.

Information about the system's current water rate structure allows the State to determine whether there are feasible water rate changes that would result in compliance or improve water quality.

The State can use this information to determine whether the system is in compliance with the State's operator certification requirements, and to determine whether the appointment of a certified operator would result in compliance or improve water quality.

States can use this information to verify that the system is taking all practicable steps to comply with the revised MCL by January 23, 2006.

This information helps the State identify whether capital improvements are required.

The State must determine that these capital improvements cannot be completed before January 23, 2006 for the system to be eligible for an exemption.

If a system needs financial assistance to complete the necessary capital improvements, it must either have entered into an agreement (public or private) to get the assistance, or it must be reasonably likely to get the assistance from a federal or State source during the period of the exemption. The Drinking Water State Revolving Fund (**DWSRF**) and the Rural Utilities Service (**RUS**) are major sources of financial assistance.

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Other sources include Community Block Grants through Housing and Urban Development Assistance and other State programs.

The system should include documentation that supports its claim, such as a letter from the State identifying the system's position on the DWSRF priority list.

If financial assistance is needed, the system should identify the source of assistance, the date the system applied for assistance, and the system's contact in the assistance organization. This information will allow the State to determine whether the system is eligible for receiving an exemption.

Alternatively, a system may choose to enter into an **"enforceable agreement"** to become part of a regional PWS.

States should work with each system receiving an exemption to develop realistic compliance schedules that require compliance as **"expeditiously as practicable."**

Systems should provide an estimate of the time they need to secure funding, finish the needed capital improvement(s), and begin operating in compliance with the revised MCL. States can use these estimates, along with their understanding of similar capital improvement projects, to develop realistic compliance schedules for the systems.

The State can use this information as a basis for determining whether a system that began operating after January 23, 2006 is eligible for an exemption. These systems are eligible for an exemption only if they can demonstrate that another source of drinking water with lower arsenic levels cannot reasonably be found.

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FORM #2: Example State Determination Form PAGE 1 OF 3

1 SYSTEM NAME	6 DATE BEGAN OPERATING
2 POP. SERVED PWSID	7 REQUEST DATE
3 SYSTEM CONTACT	8 DATE GRANTED
4 PHONE NUMBER	9 PUBLIC HEARING DATE
5 CONTACT ADDRESS	10 EXEMPTION COMPLIANCE DATE

ELIGIBILITY DETERMINATION CRITERIA INFORMATION SOURCE

11 Are there compelling factors that will prevent the system from complying by 1/23/06?

YES NO* Sanitary Survey DWSRF Application Capacity Assessment Exemption Request Other:

12 Did the system begin operating before 2/22/02? YES NO

(see 12a)

Sanitary Survey DWSRF Application Capacity Assessment Exemption Request Other:

12a. If the system began operating after 2/22/02, does the system have a reasonable alternative source of drinking water?

YES* NO Sanitary Survey DWSRF Application Capacity Assessment Exemption Request Other:

13 What is the system's high value for arsenic in finished water (in pb)?

Sanitary Survey DWSRF Application Capacity Assessment Exemption Request Other:

How many years will it take the system to achieve compliance(from 1/2001)?

Sanitary Survey DWSRF Application Capacity Assessment Exemption Request Other:

What is the product of the high arsenic value minus 10 and the years until compliance (in ppb x years)?

14 Can the system reasonably make any of the following changes with the result being compliance or improved water quality?**

YES* NO Sanitary Survey DWSRF Application Capacity Assessment Exemption Request Other:

- Rate Increases
- Accounting Changes
- Appointment of State-certified Operator
- Joint Operation
- Capacity Development Activities
- Ownership Changes
- Consolidation

15 DETERMINATION

YES – SYSTEM IS ELIGIBLE

NO – SYSTEM IS NOT ELIGIBLE

* System is not eligible for an exemption. **Given the potential availability of federal and State financial assistance.

APPROVAL DETERMINATION CRITERIA INFORMATION

SOURCE PAGE 2 OF 3

16 Has the system received a small system variance for the arsenic standard?

YES* NO Sanitary Survey WSRF Application Capacity Assessment
Exemption Request Other:

17 Is the system taking all practicable steps to meet the MCL?

YES NO* Sanitary Survey DWSRF Application Capacity Assessment
Exemption Request Other:

18a Does the system need to make capital improvements that cannot be completed before /23/06?

YES NO* Sanitary Survey DWSRF Application Capacity Assessment
Exemption Request Other:

18b Does the system need financial assistance for capital improvements?

YES (see 18c)
NO (skip to 20)

18c Is one of the following true:

- The system agreed to become part of a regional PWS?
- The system is reasonably likely to get financial assistance during the exemption?

YES (see 19)

NO* Sanitary Survey DWSRF Application Capacity Assessment
Exemption Request Other:

19 Financial assistance information. Source: DWSRF RUS Other:

Date Applied:

Source Contact:

20 DETERMINATION YES – EXEMPTION GRANTED NO – EXEMPTION DENIED

* System is not eligible for an exemption.

Approved by: _____ **Date:** _____

FORM #2: Example State Determination Form PAGE 3 OF 3

**EXEMPTION EXTENSION
CRITERIA INFORMATION SOURCE**

21 Has the system qualified for a 3 year exemption? YES NO***

22 Does the system serve fewer than 3,300 people? YES NO***

23 Does the system need financial assistance? YES NO***

24 Has the system agreed to become part of a regional PWS? YES* NO**

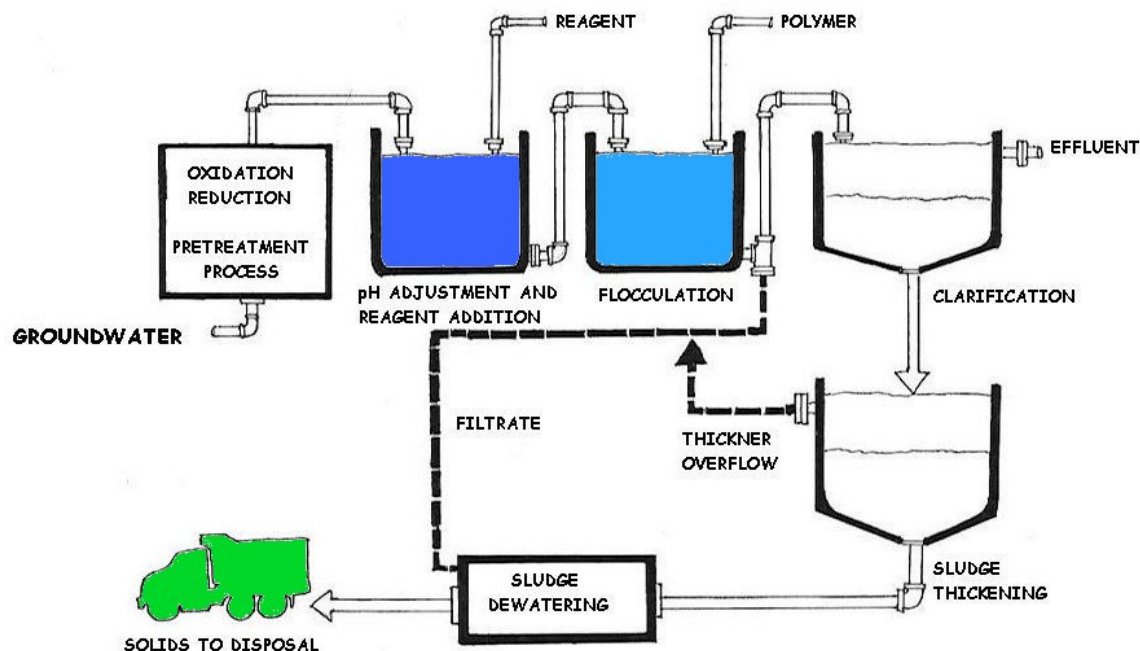
25 DETERMINATION YES – EXTENSION APPROVED NO – EXTENSION DENIED

**If yes, how many extensions and for how many total years
(not to exceed 6): Extensions Years**

*** System is not eligible for an extension.

Approved by: _____ Date: _____

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PRECIPITATION / COPRECIPITATION SYSTEM

How Can I Prevent Arsenic Accumulation in My Distribution System?

There are a number of management techniques that can be used to help keep arsenic levels low in the distribution system. They include:

- Optimize treatment operations for turbidity removal.
- Check finished water pH and alkalinity after arsenic treatment is installed. If they have changed, consider whether corrosion control practices need to be modified.
- Adopt a unidirectional flushing program for water mains.
- Clean and maintain your storage tank(s).
- Optimize distribution system operations to minimize water age. This practice will prevent sediment accumulation and water quality deterioration.
- Operate valves and hydrants to avoid sudden changes in flow direction or velocity. This practice will prevent the resuspension of sediments into the water column.
- Monitor arsenic levels at drinking water taps, hydrants, and low flow dead-end areas.

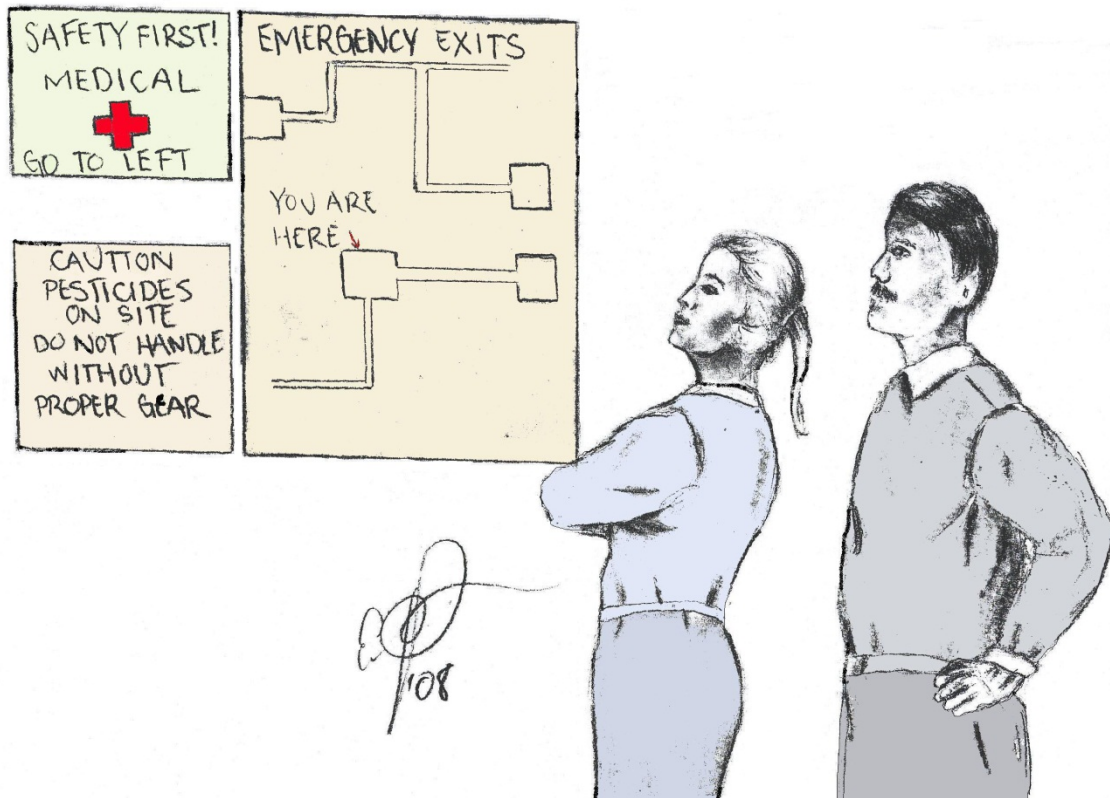
Arsenic Treatment Methods



Brake Fern

A Phytoremediation method.

Hyperaccumulating ferns have been used in the remediation of arsenic-contaminated soil, waste, and water. The fern can tolerate as much as 1,500 parts per million (ppm) of arsenic in soil, and can have a bioconcentration factor up to 265. The arsenic concentration in the plant can be as high as 2 percent (dry weight) (Ref. 15.3, 15.6).



Arsenic Can Build Up on and Release in Pipes and Storage Tanks

Public water systems with arsenic in their raw water may find that scales on pipes and other components in their distribution systems contain relatively high arsenic concentrations. These arsenic-rich scales can become dislodged and suspended in the water, and may be ultimately delivered to consumers.

Arsenic has been shown to attach to iron in distribution system pipes. Because iron is so effective at binding with arsenic, corrosion deposits can have high concentrations of arsenic solids. In a recent study, arsenic levels found in solids that were collected after pipe sections and hydrants were flushed were as high as 13.65 milligrams of arsenic per gram of solid. Most of the remaining solid was composed of iron.

Who Needs to Know about Arsenic Treatment Technologies?

This course was prepared to provide information on the current state of arsenic treatment for soil, waste, and water.

The course may be used to:

- Identify proven and effective arsenic treatment technologies.
- Screen those technologies based on effectiveness, treatment goals, application-specific characteristics, and cost.
- Apply experience from sites with similar treatment challenges.
- Find more detailed arsenic treatment information.

This course may be used by remediation site managers, hazardous waste generators (for example, wood treaters, herbicide manufacturers, mine and landfill operators), drinking water treatment plant designers and operators, and the general public to help screen arsenic treatment options.

Arsenic is a common inorganic element found widely in the environment. It is in many industrial products, wastes, and wastewaters, and is a contaminant of concern at many remediation sites.

Arsenic contaminated soil, waste, and water must be treated by removing the arsenic or immobilizing it.

Because arsenic readily changes valence states and reacts to form species with varying toxicity and mobility, effective, long-term treatment of arsenic can be difficult.



In some disposal environments arsenic has leached from arsenic-bearing wastes at high concentrations (Ref. 2.11). Recently, the EPA reduced the maximum contaminant level (**MCL**) for arsenic in drinking water from 0.050 mg/L to 0.010 mg/L, effective in 2006 (Ref. 2.9).

Drinking water suppliers may need to add new treatment processes or retrofit existing treatment systems to meet the revised MCL. In addition, it may affect Superfund remediation sites and other sites that base cleanup goals on the arsenic drinking water MCL.

This course provides information needed to help meet the challenges of arsenic treatment.

BACKGROUND

Where Does Arsenic Come From?

Arsenic occurs naturally in rocks, soil, water, air, plants, and animals.

Natural activities such as volcanic action, erosion of rocks, and forest fires, can release arsenic into the environment. Industrial products containing arsenic include wood preservatives, paints, environment include mining and smelting operations; agricultural applications; burning of fossil fuels and wastes; pulp and paper production; cement manufacturing; and former agricultural uses of arsenic(Ref. 2.1).

What Are the Health Effects of Arsenic?

Many studies document the adverse health effects in humans exposed to inorganic arsenic compounds. A discussion of those effects is available in the following documents:

- National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring (66 FR 6976 /January 22, 2001) (Ref. 2.1)
- The Agency for Toxic Substances and Disease Registry (**ATSDR**) ToxFAQs™ for Arsenic (Ref.2.13).

How Does Arsenic Chemistry Affect Treatment?

Arsenic is a metalloid or inorganic semiconductor that can form inorganic and organic compounds. It occurs with valence states of -3, 0, +3 (arsenite), and +5 (arsenate).

However, the valence states of -3 and 0 occur only rarely in nature. This discussion of arsenic chemistry focuses on inorganic species of As(III) and As(V). Inorganic compounds of arsenic include hydrides (e.g., arsine), halides, oxides, acids, and sulfides (Ref. 2.4).

The toxicity and mobility of arsenic varies with its valence state and chemical form. Arsenite and arsenate are the dominant species in surface water and sea water, and organic arsenic species can be found in natural gas and shale oil (Ref. 2.12). Different chemical compounds containing arsenic exhibit varying degrees of toxicity and solubility.

Arsenic readily changes its valence state and chemical form in the environment. Some conditions that may affect arsenic valence and speciation include (Ref. 2.7):

- pH - in the pH range of 4 to 10, As(V) species are negatively charged in water, and the predominant As(III) species is neutral in charge
- redox potential
- the presence of complexing ions, such as ions of sulfur, iron, and calcium
- microbial activity

Adsorption-desorption reactions can also affect the mobility of arsenic in the environment. Clays, carbonaceous materials, and oxides of iron, aluminum, and manganese are soil components that may participate in adsorptive reactions with arsenic (Ref. 2.7).The unstable nature of arsenic species may make it difficult to treat or result in treated wastes whose toxicity and mobility can change under some environmental conditions. Therefore, the successful treatment and long-term disposal of arsenic requires an understanding of arsenic chemistry and the disposal environment.

How Often Does Arsenic Occur in Drinking Water?

Arsenic is a fairly common environmental contaminant.

Both groundwater (e.g., aquifers) and surface water (e.g., lakes and rivers) sources of drinking water can contain arsenic. The levels of arsenic are typically higher in groundwater sources.

Arsenic levels in groundwater tend to vary geographically. In the U.S., Western states (AK, AZ, CA, ID, NV, OR, UT, and WA) tend to have the highest concentrations (>0.010 mg/L), while states in the North Central (MT, ND, SD, WY), Midwest Central (IL, IN, IA, MI, MN, OH, and WI), and New England (CT, MA, ME, NH, NJ, NY, RI, and VT) regions tend to have low to moderate concentrations (0.002 to 0.010 mg/L).

However, some portions of these areas may have no detected arsenic in drinking water.

Other regions of the U.S. may have isolated areas of high concentration. The EPA estimates that 4,000 drinking water treatment systems may require additional treatment technologies, a retrofit of existing treatment technologies, or other measures to achieve the revised MCL for arsenic.

An estimated 5.4% of community water systems (**CWSs**) using groundwater as a drinking water source and 0.7% of CWSs using surface water have average arsenic levels above 0.010 mg/L. (Ref. 2.1)

How Often Does Arsenic Occur at Hazardous Waste Sites?

Hazardous waste sites fall under several clean-up programs, such as Superfund, Resource Conservation and Recovery Act (**RCRA**) corrective actions, and state cleanup programs.

This section contains information on the occurrence and treatment of arsenic at National Priorities List (**NPL**) sites, known as Superfund sites. Information on arsenic occurrence and treatment at Superfund sites was compiled from the CERCLIS 3 database (Ref. 2.3), the Superfund NPL Assessment Program (**SNAP**) database, and the database supporting the document "*Treatment Technologies for Site Cleanup: Annual Status Course (Tenth Edition)*" (Ref.2.8).

The information sources identified for this course does not contain information on arsenic occurrence and treatment at RCRA corrective action and state cleanup program sites.

Table 2.1 lists the number of Superfund sites with arsenic as a contaminant of concern by media.

Groundwater and soil were the most common media contaminated with arsenic at 380 and 372 sites, respectively.

The number of sites in Table 2.1 exceeds the number of total sites with arsenic contamination (568) because each site may have more than one type of media contaminated with arsenic.

Table 2.1

Number of Superfund Sites with Arsenic as a Contaminant of Concern by Media

Media Type Number of Sites

Groundwater 380	Leachate 24
Soil 372	Other 21
Sediment 154	Liquid Waste 12
Surface Water 86	Air 8
Debris 77	Residuals 1
Sludge 45	Source: Ref. p65
Solid Waste 30	

Arsenic occurs frequently at NPL sites. Table 2.1 shows the most common contaminants of concern present at Superfund sites for which a Record of Decision (**ROD**) has been signed, through FY 1999, the most recent year for which such information is available.

Arsenic is the second most common contaminant of concern (after lead), occurring at 568 sites (47% of all sites on the NPL with RODs).

Table 2.2

Number of Superfund Sites with Arsenic as a Contaminant of Concern by Site

Landfills and Other Disposal 209
Chemicals and Allied Products 42
Lumber and Wood Products 33
Groundwater Plume Site 26
Metal Fabrication and Finishing 20
Batteries and Scrap Metal 18
Military and Other Ordnance 18
Transportation Equipment 15
Primary Metals Processing 14
Chemicals and Chemical Waste 12
Ordnance Production 12
Electrical Equipment 11
Radioactive Products 9
Product Storage and Distribution 8
Waste Oil and Used Oil 8
Metals 6
Drums and Tanks 6
Transportation 5
Research and Development 5
Other a 104

Sources: Ref. 2.3, 2.15

a Includes site types with fewer than 5 sites, sites whose site types were identified as "other" or "multiple", and unspecified industrial waste facilities.

b Some sites have more than one site type.

Different Arsenic Treatment Technologies

- Phytoremediation
- Electrokinetics
- Biological Treatment
- Permeable Reactive Barriers
- Ion Exchange
- Adsorption
- Membrane Filtration
- Precipitation/Coprecipitation
- In Situ Soil Flushing
- Pyrometallurgical Recovery
- Soil Washing/Acid Extraction
- Vitrification
- Solidification/Stabilization



Number of Applications of Arsenic Treatment Technologies at Superfund Sites

Information on the application of groundwater pumps and treatment technologies, including precipitation/coprecipitation, membrane filtration, adsorption, and ion exchange, is based on available data and is not comprehensive.

Methodology

This Introduction describes the purpose of the report, presents background information, and summarizes the methodology used to gather and analyze data.

Each technology described includes a brief description of the technology, information about how it is used to treat arsenic, its status and scale, and available cost and performance data, including the amount and type of soil, waste, and water treated and a summary of the results of analyses of untreated soil, waste, and water and treatment residuals for total and leachable arsenic concentrations.

The technology summaries are organized as follows: the technologies typically used to treat soil and waste appear first, in the order of their frequency of full-scale applications, followed by those typically used for water in the same order, and then by those used to treat soil, waste, and water.

These technologies have been used at full scale for the treatment of arsenic in soil, waste, and water. For the purposes of this report, the term “**soil**” includes soil, debris, sludge, sediments, and other solid-phase environmental media.

Waste includes nonhazardous and hazardous solid waste generated by industry. Water includes groundwater, drinking water, non-hazardous and hazardous industrial wastewater, surface water, mine drainage, and leachate.

Treatment Trains

Treatment trains consist of two or more technologies used together, either integrated into a single process or operated as a series of treatments in sequence.

The technologies in a train may treat the same contaminant. The information gathered for this report included many projects that used treatment trains.

A common treatment train used for arsenic in water includes an oxidation step to change arsenic from As(III) to its less soluble As(V) state, followed by precipitation/coprecipitation and filtration to remove the precipitate.

Some trains are employed when one technology alone is not capable of treating all of the contaminants. For example, at the Baird and McGuire Superfund Site (Table 9.1), an above-ground system consisting of air stripping, metals precipitation, and activated carbon adsorption was used to treat groundwater contaminated with volatile organic compounds (**VOCs**), arsenic, and semivolatile organic compounds (**SVOCs**). In this treatment train the air stripping was intended to treat VOCs; the precipitation, arsenic; and the activated carbon adsorption, SVOCs and any remaining VOCs.

In many cases, the available information does not specify the technologies within the train that are intended to treat arsenic. Influent and effluent concentrations, where available, often were provided for the entire train, and not the individual components.

In such cases, engineering judgment was used to identify the technology that treated arsenic.

For example, at the Greenwood Chemical Superfund site a treatment train consisting of metals precipitation, filtration, UV oxidation and carbon adsorption was used to treat groundwater contaminated with arsenic, VOCs, halogenated VOCs, and SVOCs.

The precipitation and filtration were assumed to remove arsenic, and the UV oxidation and carbon adsorption were assumed to have only a negligible effect on the arsenic concentration.

Where a train included more than one potential arsenic treatment technology, all arsenic treatment technologies were assumed to contribute to arsenic treatment, unless available information indicated otherwise.

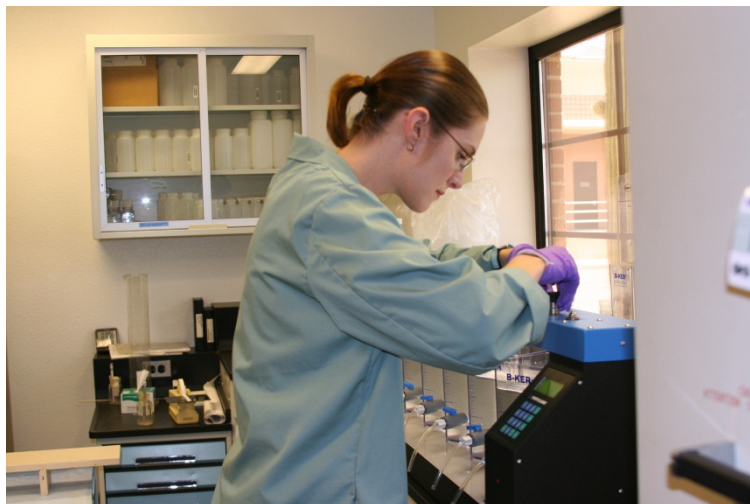
For example, at the Higgins Farm Superfund site, arsenic contaminated groundwater was treated with precipitation and ion exchange.

Activated carbon adsorption is most commonly used to treat organic contaminants.

This technology is generally ineffective on As(III) (Ref. 2.14). Where treatment trains included activated carbon adsorption and another arsenic treatment technology, it was assumed that activated carbon adsorption did not contribute to the arsenic treatment, unless the available information indicated otherwise.

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***A Bangladeshi shows the lesions from arsenicosis
(photo by WPI/M. Smith-Nilson)***

Comparison of Arsenic Treatment Technologies

What Technologies Are Used to Treat Arsenic?

This section identifies 13 technologies applicable to arsenic-contaminated soil, waste, and water. Technologies are considered applicable if they have been used at full scale to treat arsenic.

The media treated by these technologies can be grouped into two general categories: soil and waste; and water.

Technologies applicable to one type of soil and waste are typically applicable to other types. For example, solidification/stabilization has been used to effectively treat industrial waste, soil, sludge, and sediment.

Similarly, technologies applicable to one type of water are generally applicable to other types. For example, precipitation/coprecipitation has been used to effectively treat industrial wastewaters, groundwater, and drinking water.

Arsenic Treatment Technologies

Soil and Waste Treatment Technologies

- Solidification/Stabilization (S/S)
- Vitrification
- Soil Washing/Acid Extraction
- Pyrometallurgical Recovery
- In Situ Soil Flushing

Water Treatment Technologies

- Precipitation/Coprecipitation
- Membrane Filtration
- Adsorption
- Ion Exchange
- Permeable Reactive Barriers

Soil, Waste, and Water Treatment Technologies

- Electrokinetics
- Phytoremediation
- Biological Treatment



What Technologies Are Used Most Often to Treat Arsenic?

This section provides information on the number of treatment projects identified for each technology and estimates of the relative frequency of their application.

The most frequently used technology for soil and waste containing arsenic is solidification/stabilization. The available data show that this technology can effectively meet regulatory cleanup levels, is commercially available to treat both soil and waste, is usually less expensive, and generates a residual that typically does not require further treatment prior to disposal.

Other arsenic treatment technologies for soil and waste are typically used for specific applications.

Vitrification may be used when a combination of contaminants are present that cannot be effectively treated using solidification/stabilization. It has also been used when the vitrification residual could be sold as a commercial product.

However, vitrification typically requires large amounts of energy, can be more expensive than S/S, and may generate off-gasses containing arsenic.

Soil washing/acid extraction is used primarily to treat soil. However, it is not applicable to all types of soil or to waste.

Pyrometallurgical treatment has been used primarily to recycle arsenic from industrial wastes containing high concentrations of arsenic from metals refining and smelting operations. These technologies may not be applicable to soil and waste containing low concentrations of arsenic. In situ soil flushing treats soil in place, eliminating the need to excavate soil.

However, no performance data were identified for the limited number of full-scale applications of this technology to arsenic.

For water containing arsenic, the most frequently used technology is precipitation/coprecipitation. Based on the information gathered for this report, precipitation/coprecipitation is frequently used to treat arsenic contaminated water, and is capable of treating a wide range of influent concentrations to the revised MCL for arsenic.

The effectiveness of this technology is less likely to be reduced by characteristics and contaminants other than arsenic, compared to other water treatment technologies. It is also capable of treating water characteristics or contaminants other than arsenic, such as hardness or heavy metals.

Systems using this technology generally require skilled operators; therefore, precipitation/ coprecipitation is more cost effective at a large scale where labor costs can be spread over a larger amount of treated water produced.

The effectiveness of adsorption and ion exchange for arsenic treatment is more likely than precipitation/coprecipitation to be affected by characteristics and contaminants other than arsenic.

EPA Water Treatment Processes Section

Treating your water to reduce arsenic will be necessary if more cost-effective alternatives are not available. EPA has identified best available technologies (BATs) and small system compliance technologies (SSCTs) for removing arsenic from drinking water (40 CFR 141.62(c)&(d)).

BATs are technologies that have proven effective for large systems, and SSCTs are technologies that are effective and affordable for small systems. Systems are not required to use any specific technology. Systems can use technologies not listed as BATs or SSCTs if they are effective. Installing a BAT makes a system eligible for a general variance if, due to source water conditions, the system cannot achieve compliance. A general variance, if approved by the State, would allow the system to supply water with an arsenic level above the MCL for a certain period of time.

EPA anticipates that most small systems will use activated alumina (or another type of adsorptive media), reverse osmosis POU devices, or modified lime softening. For more information on these technologies. Most technologies may require pre-treatment (e.g., chlorination) to effectively remove arsenic from drinking water. The need for pre-treatment depends on source water quality.

You may also wish to consider promising technologies such as granular ferric hydroxide and modified activated alumina, which are not yet approved by EPA as BATs or SSCTs. EPA has developed the Arsenic Treatment Technology Design Manual for Small Systems (EPA 816-R-02-011), which examines these new technologies, as well as the BATs and SSCTs. This manual is available from EPA by calling the Safe Drinking Water Hotline at 1-800-426-4791 or by going on line at www.epa.gov/safewater.

Activated Alumina

Activated alumina (AA), an adsorptive medium, uses very small grains, which are packed into a large container. Water is then continuously passed through one or more containers. When AA is exhausted it is simply disposed of and replaced with fresh AA. AA can treat water containing up to 0.160 mg/L of arsenic.

Reverse Osmosis

Reverse osmosis uses high pressure to force water through a membrane with microscopic holes that prevents arsenic and other large contaminants from passing through. Some water is also not able to pass through the membrane and is wasted. Reverse osmosis can treat water containing up to 0.160 mg/L of arsenic.

Modified Lime Softening

The addition of lime to water causes calcium and magnesium to form solid particles, which can then be removed by clarification and filtration. Arsenic can join these particles and be removed along with them. Lime softening is very expensive and water systems are unlikely to install this technology only for arsenic removal. However, for water systems that use lime softening to reduce hardness, the process can be modified to increase arsenic removal. Modified lime softening can treat water containing up to 0.080 mg/L of arsenic.

Point-of-Use Units

Under the Arsenic Rule, systems have another approach available for achieving compliance. This approach involves system-installed and maintained POU devices on a single tap in each customer's household. If you choose this approach, your system will have to arrange for regular inspection and maintenance of the devices. You, not the homeowner, are responsible for maintaining the POU device.

Either system staff or service providers under contract with the system must regularly inspect and service each device. You will need to establish and maintain an especially good working relationship with your customers if you choose POU devices. Your employees or contractors will need to enter customers' homes on a regular basis. Customers may be willing to accept this inconvenience because POU devices may be much less expensive than central treatment.

Currently, EPA considers only activated alumina and reverse osmosis POU devices to be POU SSCTs for arsenic removal. Point-of-use reverse osmosis treatment unit EPA is developing guidance on how to implement a POU compliance strategy. You should consult with your State to determine whether a POU compliance strategy can work for you.

Central Treatment

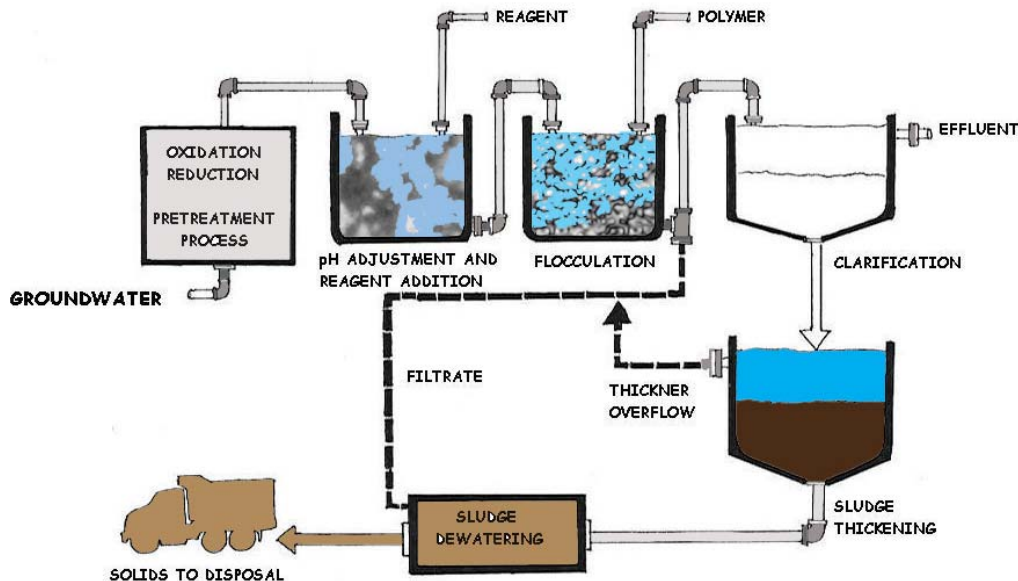
- ✓ All water treated
- ✓ Less expensive for large communities
- ✓ Capital costs very high, but equipment lasts a long time
- ✓ Little customer involvement
- ✓ Does not require access to individual homes
- ✓ Some technologies require a highly trained operator
- ✓ Waste disposal may be expensive

Point-of-Use Units

- ✓ Treats water at the individual taps where the unit is installed
- ✓ Can be less expensive for small communities
- ✓ Capital costs low, but media and membranes may require frequent replacement
- ✓ Much customer involvement and support necessary
- ✓ Requires access to individual homes
- ✓ Does not require a highly trained operator; maintenance can be contracted out
- ✓ Waste disposal typically not a problem

Precipitation/Coprecipitation Process

- Oxidation/Reduction
- (Pretreatment Process)
- Groundwater Solids to
- Disposal
- Sludge
- Dewatering
- Filtrate
- Thickening
- Thickener
- Overflow
- Flocculation pH Adjustment and
- Reagent Addition
- Polymer Reagent
- Effluent
- Clarification



Model of a Precipitation/Coprecipitation System

Precipitation/coprecipitation has been the most frequently used method to treat arsenic contaminated water, including groundwater, surface water, leachate, mine drainage, drinking water, and wastewater in numerous pilot- and full-scale applications. Based on the information collected to prepare this report, this technology typically can reduce arsenic concentrations to less than 0.050 mg/L and in some cases has reduced arsenic concentrations to below 0.010 mg/L.

Technology Description: Precipitation uses chemicals to transform dissolved contaminants into an insoluble solid. In coprecipitation, the target contaminant may be dissolved or in a colloidal or suspended form. Dissolved contaminants do not precipitate, but are adsorbed onto another species that is precipitated.

Colloidal or suspended contaminants become enmeshed with other precipitated species, or are removed through processes such as coagulation and flocculation.

Many processes to remove arsenic from water involve a combination of precipitation and coprecipitation. The precipitated/coprecipitated solid is then removed from the liquid phase by clarification or filtration. Arsenic precipitation/coprecipitation can use combinations of the chemicals and methods listed below.

Media Treated:

- Drinking water
- Groundwater
- Wastewater
- Surface water
- Leachate
- Mine drainage

Chemicals and Methods Used for Arsenic Precipitation/Coprecipitation:

- Ferric salts, (e.g., ferric chloride), ferric sulfate, ferric hydroxide
- Ammonium sulfate
- Alum (aluminum hydroxide)
- pH adjustment
- Lime softening, limestone, calcium hydroxide
- Manganese sulfate
- Copper sulfate
- Sulfide



Technology Description and Principles

For this report, technologies were considered precipitation/coprecipitation if they involved the following steps:

- Mixing of treatment chemicals into the water
- Formation of a solid matrix through precipitation, coprecipitation, or a combination of these processes, and
- Separation of the solid matrix from the water

Technologies that remove arsenic by passing it through a fixed bed of media, where the arsenic may be removed through adsorption, precipitation/coprecipitation, or a combination of these processes, are discussed in the adsorption treatment section.

Precipitation/coprecipitation usually involves pH adjustment and addition of a chemical precipitant or coagulant; it can also include addition of a chemical oxidant. Oxidation of arsenic to its less soluble As(V) state can increase the effectiveness of precipitation/coprecipitation processes, and can be done as a separate pretreatment step or as part of the precipitation process. Some pretreatment processes that oxidize As(III) to As(V) include ozonation, photo oxidation, or the addition of oxidizing chemicals such as potassium permanganate, sodium hypochlorite, or hydrogen peroxide.

Clarification or filtration is commonly used to remove the solid precipitate. Precipitation/coprecipitation is frequently used to treat water contaminated with metals.

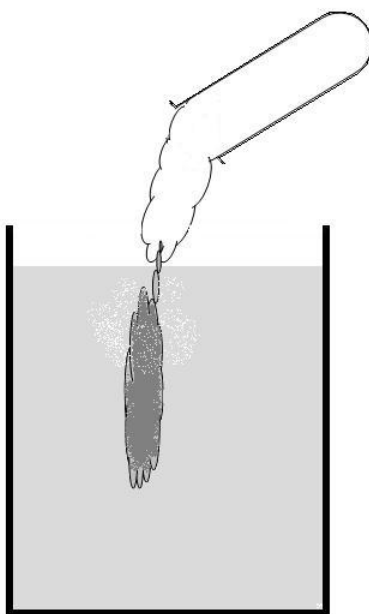
The references identified for this report contained information on its application to industrial wastewater, groundwater, surface water, leachate, and mine drainage.

Precipitation/Coprecipitation Chemistry

Precipitation Reactions

A **precipitate** is a solid that forms out of solution.

A common example of a precipitation reaction happens when mixing the following two clear solutions:



Solvent + Solute = Solution

Silver nitrate (AgNO_3) + Sodium chloride (NaCl) = AgCl precipitate

The chemical equation for this reaction is ...



The precipitate forms because the solid product of the reaction (AgCl) is **insoluble** in water.

That is true for all precipitates - the solids are insoluble in aqueous solutions.

Precipitation reactions occur all around us. For example, sometimes the pipes in our homes get clogged because precipitates of magnesium and calcium oxides have deposited themselves within the pipes. This can happen with "**hard**" water.

Another example is a kidney stone. A kidney stone is nothing more than a precipitate - often of calcium ions (from cheese) and oxalates. It is often suggested that a good way to avoid kidney stones is to drink a lot of water. This helps because the solubility of the precipitate increases with the amount of water - thus avoiding the formation of the kidney stone to begin with.

Complex

The chemistry of precipitation/coprecipitation is often complex, and depends upon a variety of factors, including the speciation of arsenic, the chemical precipitants used and their concentrations, the pH of the water, and the presence of other chemicals in the water to be treated. As a result, the particular mechanism that results in the removal of arsenic through precipitation/coprecipitation treatment is process-specific, and in some cases is not completely understood.

For example, the removal mechanism in the treatment of As(V) with Fe(III) has been debated in the technical literature. It is beyond the scope of this course to provide all possible chemical reactions and mechanisms for precipitation/coprecipitation processes that are used to remove arsenic. More detailed information on the chemistry involved in specific processes can be found in the references listed at the end of this section.

The effectiveness of this technology can be evaluated by comparing influent and effluent contaminant concentrations. All of the 12 environmental media projects for which both influent and effluent arsenic concentration data were available had influent concentrations greater than 0.050 mg/L.

The treatments achieved effluent concentrations of less than 0.050 mg/L in eight of the projects and less than 0.010 mg/L in four of the projects. Information on the leachability of arsenic from the precipitates and sludges was available for three projects. For all of these projects, the concentration of leachable arsenic as measured by the toxicity characteristic leaching procedure (TCLP) (the RCRA regulatory threshold for identifying a waste that is hazardous because it exhibits the characteristic of toxicity for arsenic) was below 5.0 mg/L.

Factors Affecting Precipitation/Coprecipitation Performance

- **Valence state of arsenic** - The presence of the more soluble trivalent state of arsenic may reduce the removal efficiency. The solubility of arsenic depends upon its valence state, pH, the specific arsenic compound, and the presence of other chemicals with which arsenic might react (Ref. 9.12). Oxidation to As(V) could improve arsenic removal through precipitation/coprecipitation (Ref. 9.7).
- **pH** - In general, arsenic removal will be maximized at the pH at which the precipitated species is least soluble. The optimal pH range for precipitation/coprecipitation depends upon the waste treated and the specific treatment process (Ref. 9.7).
- **Presence of other compounds** - The presence of other metals or contaminants may impact the effectiveness of precipitation/coprecipitation. For example, sulfate could decrease arsenic removal in processes using ferric chloride as a coagulant, while the presence of calcium or iron may increase the removal of arsenic in these processes (Ref. 9.7).

Case Study: Winthrop Landfill Site

The Winthrop Landfill Site, located in Winthrop, Maine, is a former dump site that accepted municipal and industrial wastes. Groundwater at the site was contaminated with arsenic and chlorinated and nonchlorinated VOCs.

A pump-and-treat system for the groundwater has been in operation at the site since 1995.

Organic compounds have been remediated to below action levels, and the pump and-treat system is currently being operated for the removal of arsenic alone. The treatment train consists of equalization/pH adjustment to pH 3, chemical oxidation with hydrogen peroxide, precipitation/coprecipitation via pH adjustment to PH 7, flocculation/clarification, and sand bed filtration.

It treats 65 gallons per minute of groundwater containing average arsenic concentrations of 0.3 mg/L to below 0.005 mg/L.

Through May, 2001, 359 pounds of arsenic had been removed from groundwater at the Winthrop Landfill Site using this above ground treatment system. Capital costs for the system were about \$2 million, and O&M costs are approximately \$250,000 per year (Ref. 9.29, cost year not provided).

Of the 12 drinking water projects having both influent and effluent arsenic concentration data, eight had influent concentrations greater than 0.050 mg/L. The treatments achieved effluent concentrations of less than 0.050 mg/L in all eight of these projects, and less than 0.010 mg/L in two projects. Information on the leachability of arsenic from the precipitates and sludges was available for six projects. For these projects the leachable concentration of arsenic was below 5.0 mg/L.

All of the 28 wastewater projects having both influent and effluent arsenic concentration data had influent concentrations greater than 0.050 mg/L. The treatments achieved effluent concentrations of less than 0.050 mg/L in 16 of these projects, and less than 0.010 mg/L in 11 projects. Information on the leachability of arsenic from the precipitates and sludges was available for four projects.

Only one of these projects had a leachable concentration of arsenic below 5.0 mg/L. Projects that did not reduce effluent arsenic concentrations to below 0.050 or 0.010 mg/L do not necessarily indicate that precipitation/coprecipitation cannot achieve these levels. The treatment goal for some applications could have been above these concentrations, and the technology may have been designed and operated to meet a higher concentration.

Some projects will include treatment trains, the most common being precipitation/coprecipitation followed by activated carbon adsorption or membrane filtration. In those cases, the performance data listed are for the entire treatment train, not just the precipitation/coprecipitation step. The case study in this section discusses in greater detail the removal of arsenic from groundwater using an above-ground treatment system at the Winthrop Landfill Superfund site.

Applicability, Advantages, and Potential Limitations

Precipitation/coprecipitation is an active ex situ treatment technology designed to function with routine chemical addition and sludge removal. It usually generates a sludge residual, which typically requires treatment such as dewatering and subsequent disposal.

Some sludge from the precipitation/coprecipitation of arsenic can be a hazardous waste and require additional treatment such as solidification/stabilization prior to disposal. In the presence of other metals or contaminants, arsenic precipitation/coprecipitation processes may also cause other compounds to precipitate, which can render the resulting sludge hazardous (Ref. 9.7). The effluent may also require further treatment, such as pH adjustment, prior to discharge or reuse.

Factors Affecting Precipitation/Coprecipitation Costs

- **Type of chemical addition** - The chemical added will affect costs. For example, calcium hypochlorite, is a less expensive oxidant than potassium permanganate (Ref. 9.16).
- **Chemical dosage** - The cost generally increases with increased chemical addition. Larger amounts of chemicals added usually results in a larger amount of sludge requiring additional treatment or disposal (Ref. 9.7, 9.12).
- **Treatment goal** - Application could require additional treatment to meet stringent cleanup goals and/or effluent and disposal standards(Ref. 9.7)
- **Sludge disposal** - Sludge produced from the precipitation/coprecipitation process could be considered a hazardous waste and require additional treatment before disposal, or disposal as hazardous waste (Ref. 9.7).

More detailed information on selection and design of arsenic treatment systems for small drinking water systems is available in the document “**Arsenic Treatment Technology Design Manual for Small Systems** “ (Ref. 9.36).

Summary of Cost Data

Limited cost data are currently available for precipitation/coprecipitation treatment of arsenic. At the Winthrop Landfill Site (Project 1), groundwater containing arsenic, 1,1-dichloroethane, and vinyl chloride is being pumped and treated above ground through a treatment train that includes precipitation.

The total capital cost of this treatment system was \$2 million (\$1.8 million for construction and \$0.2 million for design). O&M costs were about \$350,000 per year for the first few years and are now approximately \$250,000 per year. The treatment system has a capacity of 65 gpm.

However, these costs are for the entire treatment train (Ref. 9.29, cost year not provided). At the power substation in Fort Walton, Florida, the reported O&M cost was \$0.006 per gallon (for the entire treatment train, Ref 9.32, cost year not provided). Capital cost information was not provided.

A low-cost, point-of-use precipitation/coprecipitation treatment designed for use in developing nations with arsenic-contaminated drinking water was pilot-tested in four areas of Bangladesh (Project 31). This simple treatment process consists of a two-bucket system that uses potassium permanganate and alum to precipitate arsenic, followed by sedimentation and filtration.

The equipment cost of the project was approximately \$6, and treatment of 40 liters of water daily would require a monthly chemical cost of \$0.20 (Ref. 9.22, cost year not provided).

The document "**Technologies and Costs for Removal of Arsenic From Drinking Water**" (Ref. 9.7) contains more information on the cost of systems to treat arsenic in drinking water to below the revised MCL of 0.010 mg/L.

The document includes capital and O&M cost curves for three precipitation/coprecipitation processes:

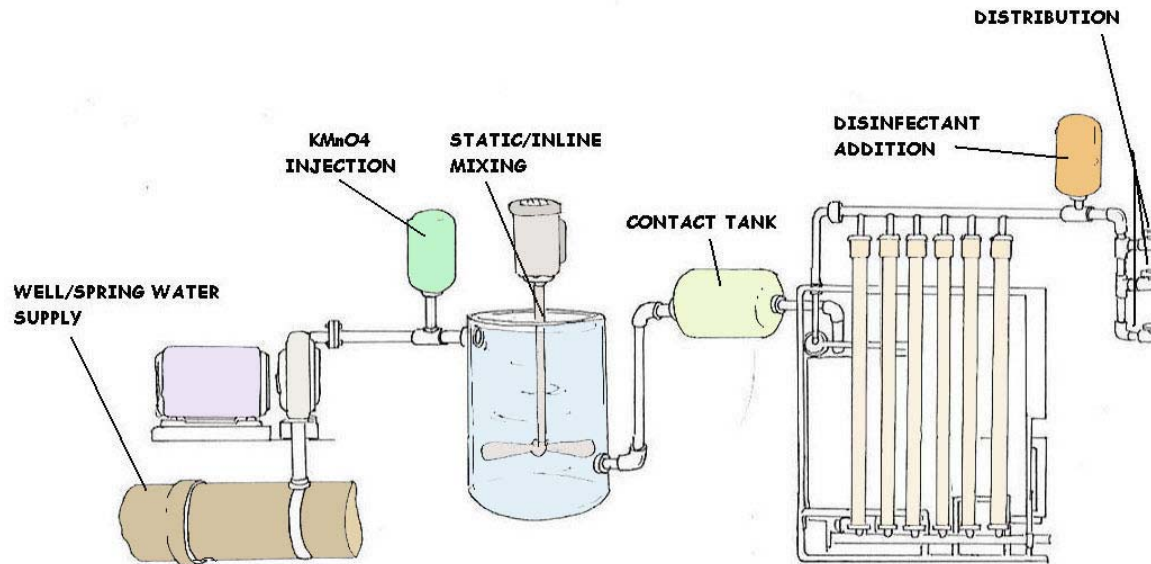
- Enhanced coagulation/filtration
- Enhanced lime softening
- Coagulation assisted microfiltration

These cost curves are based on computer cost models for drinking water treatment systems. The cost information available for enhanced coagulation/ filtration and enhanced lime softening are for retrofitting existing precipitation/coprecipitation systems at drinking water treatment plants to meet the revised MCL.

Therefore, the cost information could not be used to estimate the cost of a new precipitation/coprecipitation treatment system.



One of the steps in water treatment is softening. Lime can be added to the water, resulting in an exothermic reaction and a pH increase to 11.



ARSENIC REMOVAL SYSTEM

Arsenic Rule at a Glance

Maximum Contaminant Level

in parts per million (ppm)

MCL = 0.010 ppm

Maximum Contaminant Level Goal MCLG = 0 ppm

Health Effects

Skin damage or problems with circulatory systems, and may have increased risk of getting cancer .

Sources of contamination

Erosion of natural deposits; runoff from orchards, runoff from glass & electronic production wastes.

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Membrane Filtration for Arsenic

Membrane filtration can remove a wide range of contaminants from water. Based on the information collected to prepare this report, this technology typically can reduce arsenic concentrations to less than 0.050 mg/L and in some cases has reduced arsenic concentrations to below 0.010 mg/L.

However, its effectiveness is sensitive to a variety of untreated water contaminants and characteristics. It also produces a larger volume of residuals and tends to be more expensive than other arsenic treatment technologies.

Therefore, it is used less frequently than precipitation/coprecipitation, adsorption, and ion exchange. It is most commonly used to treat groundwater and drinking water, or as a polishing step for precipitation processes. Only two full-scale projects using membrane filtration to treat arsenic were identified in the sources researched for this course.

Technology Description: Membrane filtration separates contaminants from water by passing it through a semi-permeable barrier or membrane. The membrane allows some constituents to pass through, while blocking others (Ref. 10.2, 10.3).

Media Treated:

- Drinking water
- Groundwater
- Surface water
- Industrial wastewater

Types of Membrane Processes:

- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse osmosis

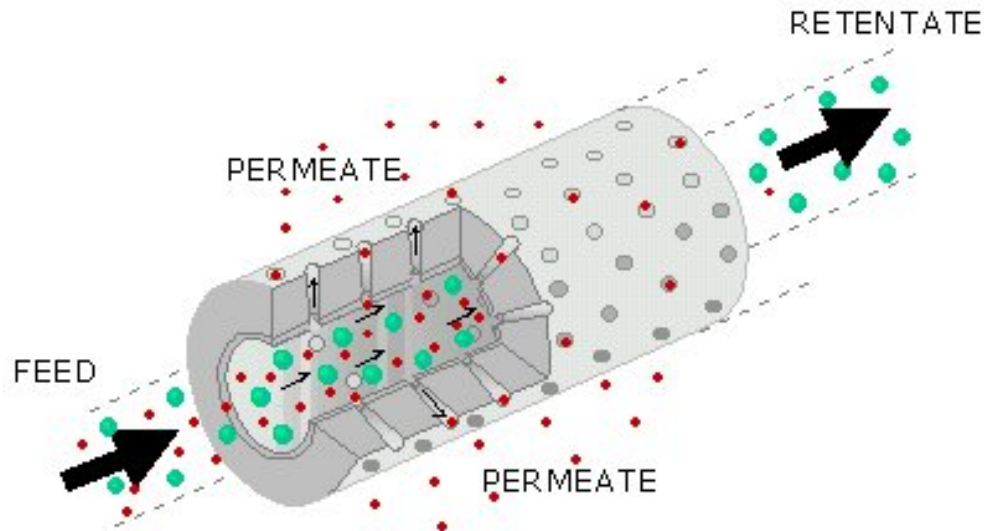
Technology Description and Principles

There are four types of membrane processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). All four of these processes are pressure-driven and are categorized by the size of the particles that can pass through the membranes or by the molecular weight cut off (i.e., pore size) of the membrane (Ref. 10.2). The force required to drive fluid across the membrane depends on the pore size; NF and RO require a relatively high pressure (50 to 150 pounds per square inch [psi]), while MF and UF require lower pressure (5 to 100 psi) (Ref.10.4). The low pressure processes primarily remove contaminants through physical sieving, and the high pressure processes through chemical diffusion across the permeable membrane (Ref. 10.4).

Because arsenic species dissolved in water tend to have relatively low molecular weights, only NF and RO membrane processes are likely to effectively treat dissolved arsenic (Ref. 10.4). MF has been used with precipitation/coprecipitation to remove solids containing arsenic. The sources used for this report did not contain any information on the use of UF to remove arsenic; therefore, UF is not discussed in this technology summary.

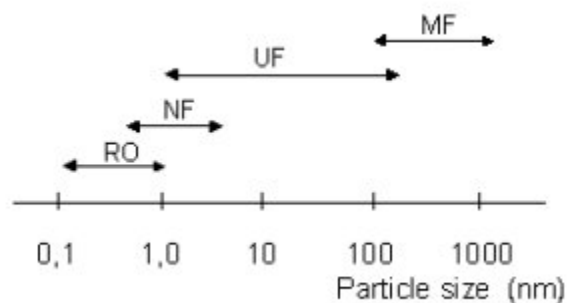
Membrane filtration processes

A membrane process is a separating process, in which a feed flow is divided into two flows, either gaseous or liquid. The flow containing the components retained by the membrane is the retentate flow, while the components passing through the membrane form the permeate flow. If the two phases are fluid, then we speak of membrane filtration.



Transport through the membrane is performed by a pressure difference, a concentration difference, a chemical or electrical potential difference as a driving force. The membrane itself forms a semi-permeable barrier through which some particles are transported faster than others, so that a separation occurs.

The pressure driven membrane filtration processes are: microfiltration (**MF**), ultrafiltration (**UF**), nanofiltration (**NF**) and reverse osmosis (**RO**). They differ primarily in the size of the particles to separate and the membranes needed for it.



The smaller the pore size of the membranes, the higher the pressure needed to achieve separation. In the case of microfiltration and ultrafiltration we speak of low pressure processes, while nanofiltration and reverse osmosis are high pressure processes.

The following table gives a summary of the different processes, including pervaporation.

Process	Driving force	Separation principle	Applications
Microfiltration	Pressure difference (0.1 - 1 bar)	filtration	bacteria filter
Ultrafiltration	Pressure difference (0.5 – 10 bar)	filtration	concentrating macromolecular solutions
Nanofiltration	Pressure difference (5 – 20 bar)	filtration/ electrostatic interaction	partial water softening
Reverse osmosis	Pressure difference (8 – 100 bar)	Solution diffusion mechanism	water desalination
Pervaporation	Concentration gradient	Solution diffusion mechanism	separating organic solvents

MF generates two treatment residuals from the influent waste stream: a treated effluent (permeate) and a rejected waste stream of concentrated contaminants (reject).

RO is a high pressure process that primarily removes smaller ions typically associated with total dissolved solids. The molecular weight cut off for RO membranes ranges from 1 to 20,000, which is a significantly lower cut off than for NF membranes. The molecular weight cut off for NF membranes ranges from approximately 150 to 20,000. NF is a high-pressure process that primarily removes larger divalent ions associated with hardness (for example, calcium [Ca], and magnesium [Mg] but not monovalent salts (for example, sodium [Na] and chlorine [Cl]).

NF is slightly less efficient than RO in removing dissolved arsenic from water (Ref. 10.4).

Factors Affecting Membrane Filtration Performance

- **Suspended solids, high molecular weight, dissolved solids, organic compounds, and colloids** - The presence of these constituents in the feed stream may cause membrane fouling.

- **Oxidation state of arsenic** - Prior oxidation of the influent stream to convert As(III) to As(V) will increase arsenic removal; As(V) is generally larger and is captured by the membrane more effectively than As(III).

- **pH** - pH may affect the adsorption of arsenic on the membrane by creating an electrostatic charge on the membrane surface.

- **Temperature** - Low influent stream temperatures decreases membrane flux. Increasing system pressure or increasing the membrane surface area may compensate for low influent stream temperature.

MF is a low-pressure process that primarily removes particles with a molecular weight above 50,000 or a particle size greater than 0.050 micrometers. The pore size of MF membranes is too large to effectively remove dissolved arsenic species, but MF can remove particulates containing arsenic and solids produced by precipitation/coprecipitation (Ref. 10.4).

Media and Contaminants Treated

Drinking water, surface water, groundwater, and industrial wastewater can be treated with this technology. Membrane filtration can treat dissolved salts and other dissolved materials (Ref. 10.12).

Summary of Performance Data

Performance results for membrane filtration are typically reported as percent removal, (i.e., the percentage of arsenic, by mass, in the influent that is removed or rejected from the influent wastewater stream). A higher percentage indicates greater removal of arsenic, and therefore, more effective treatment.

Although many of the projects listed in Table 10.1 may have reduced arsenic concentrations to below 0.05 mg/L or 0.01 mg/L, data on the concentration of arsenic in the effluent and reject streams were not available for most projects.

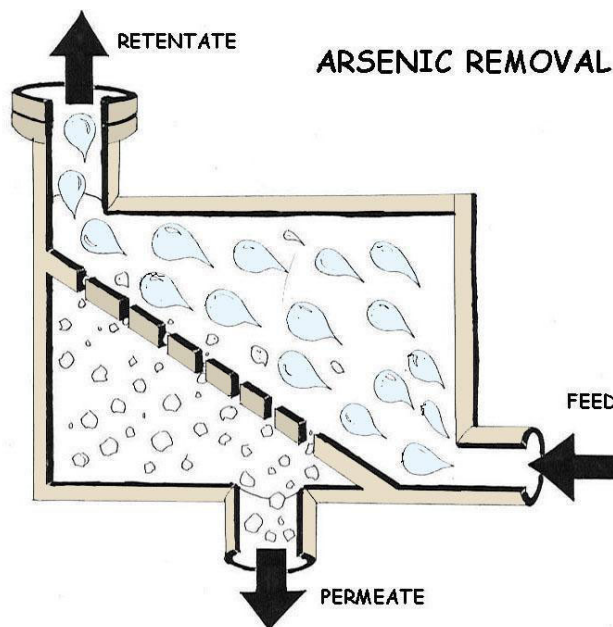
For two RO projects, the arsenic concentration in the reject stream was available, allowing the concentration in permeate to be calculated.

For both projects, the concentration of arsenic prior to treatment was greater than 0.050 mg/L, and was reduced to less than 0.010 mg/L in the treated water.

For two projects involving removal of solids from precipitation/coprecipitation treatment of arsenic with MF, the arsenic concentration in the permeate was available. The concentration prior to precipitation/coprecipitation treatment was greater than 0.050 mg/L for one project, and ranged from 0.005 to 3.8 mg/L for the other.

For both projects, the concentration in the treated water was less than 0.005 mg/L.

The case study at the end of this section further discusses the use of membrane filtration to remove arsenic from groundwater used as a drinking water source.



Case Study: Park City Spiro Tunnel Water Filtration Plant

The Park City Spiro Tunnel Water Filtration Plant in Park City, Utah treats groundwater from waterbearing fissures that collect in a tunnel of an abandoned silver mine to generate drinking water. A pilot-scale RO unit treated contaminated water at a flow rate of 0.77 gallons per minute (gpm) from the Spiro tunnel for 34 days. The total and dissolved arsenic in the feedwater averaged 0.065 and 0.042 mg/L, respectively. The total and dissolved arsenic concentrations in the permeate averaged <0.0005 and <0.0008 mg/L, respectively.

The RO process reduced As (V) from 0.035 to 0.0005 mg/L and As (III) from 0.007 to 0.0005 mg/L. The membrane achieved 99% total As removal and 98% As (V) removal (Ref. 10.12).

Factors Affecting Membrane Filtration Costs

- Type of membrane filtration - The type of membrane selected may affect the cost of the treatment (Ref. 10.1, 10.2).
- Initial waste stream - Certain waste streams may require pretreatment, which would increase costs (Ref. 10.4).
- Rejected waste stream - Based on concentrations of the removed contaminant, further treatment may be required prior to disposal or discharge (Ref. 10.4).

Applicability, Advantages, and Potential Limitations

Membrane technologies are capable of removing a wide range of dissolved contaminants and suspended solids from water (Ref. 10.12). RO and NF technologies require no chemical addition to ensure adequate separation. This type of treatment may be run in either batch or continuous mode.

This technology's effectiveness is sensitive to a variety of contaminants and characteristics in the untreated water. Suspended solids, organics, colloids, and other contaminants can cause membrane fouling.

Therefore, it is typically applied to groundwater and drinking water, which are less likely to contain fouling contaminants. It is also applied to remove solids from precipitation processes and as a polishing step for other water treatment technologies when lower concentrations must be achieved.

More detailed information on selection and design of arsenic treatment systems for small drinking water systems is available in the document "**Arsenic Treatment Technology Design Manual for Small Systems**" (Ref. 10.15).

Summary of Cost Data

The research conducted in support of this report did not document any cost data for specific membrane filtration projects to treat for arsenic. The document "**Technologies and Costs for Removal of Arsenic From Drinking Water**" (Ref. 10.4) contains additional information on the cost of point-of-use reverse osmosis systems to treat arsenic in drinking water to levels below the revised MCL of 0.010 mg/L. The document includes capital and Operating & Maintenance (**O&M**) cost curves for this technology. These cost curves are based on computer cost models for drinking water treatment systems.

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Adsorption Treatment for Arsenic

Adsorption has been used to treat groundwater and drinking water containing arsenic.

Based on the information collected for this course, this technology typically can reduce arsenic concentrations to less than 0.050 mg/L and in some cases has reduced arsenic concentrations to below 0.010 mg/L. Its effectiveness is sensitive to a variety of untreated water contaminants and characteristics. It is used less frequently than precipitation/coprecipitation, and is most commonly used to treat groundwater and drinking water, or as a polishing step for other water treatment processes.

Technology Description: In adsorption, solutes (contaminants) concentrate at the surface of a sorbent, thereby reducing their concentration in the bulk liquid phase. The adsorption media is usually packed into a column. As contaminated water is passed through the column, contaminants are adsorbed. When adsorption sites become filled, the column must be regenerated or disposed of and replaced with new media.

Media Treated:

- Groundwater
- Drinking water

Types of Sorbent Used in Adsorption to Treat Arsenic:

- Activated alumina (**AA**)
- Activated carbon (**AC**)
- Copper-zinc granules
- Granular ferric hydroxide, ferric hydroxide coated newspaper pulp, iron oxide coated sand, iron filings mixed with sand
- Greensand filtration (KMnO₄ coated glauconite)
- Proprietary media
- Surfactant-modified zeolite

Technology Description and Principles

This section discusses arsenic removal processes that use a fixed bed of media through which water is passed. Some of the processes described in this section rely on a combination of adsorption, precipitation/coprecipitation, ion exchange, and filtration.

However, the primary removal mechanism in each process is adsorption. For example, greensand is made from glauconite, a green, iron-rich, clay-like mineral that usually occurs as small pellets mixed with other sand particles. The glauconite-containing sand is treated with potassium permanganate (**KMnO₄**), forming a layer of manganese oxides on the sand.

As water passes through a greensand filtration bed, the KMnO₄ oxidizes As(III) to As(V), and As(V) adsorbs onto the greensand surface. In addition, arsenic is removed by ion exchange, displacing species from the manganese oxide (presumably hydroxide ion [OH⁻] and water [H₂O]). When the KMnO₄ is exhausted, the greensand media must be regenerated or replaced.

Greensand media is regenerated with a solution of excess KMnO₄. Greensand filtration is also known as oxidation/filtration (Ref. 11.3).

Activated alumina (**AA**) is the sorbent most commonly used to remove arsenic from drinking water (Ref. 11.1), and has also been used for groundwater (Ref. 11.4).

The reported adsorption capacity of AA ranges from 0.003 to 0.112 grams of arsenic per gram of AA (Ref. 11.4). It is available in different mesh sizes and its particle size affects contaminant removal efficiency.

Up to 23,400 bed volumes of wastewater can be treated before AA requires regeneration or disposal and replacement with new media (Ref. 11.3). Regeneration is a four-step process:

- Backwashing
- Regeneration
- Neutralization
- Rinsing

The regeneration process desorbs the arsenic. The regeneration fluid most commonly used for AA treatment systems is a solution of sodium hydroxide.

The most commonly used neutralization fluid is a solution of sulfuric acid. The regeneration and neutralization steps for AA adsorption systems might produce a sludge because the alumina can be dissolved by the strong acids and bases used in these processes, forming an aluminum hydroxide precipitate in the spent regeneration and neutralization fluids. This sludge typically contains a high concentration of arsenic (Ref. 11.1).

Activated carbon (**AC**) is an organic sorbent that is commonly used to remove organic and metal contaminants from drinking water, groundwater, and wastewater (Ref. 11.4).

AC media are normally regenerated using thermal techniques to desorb and volatilize contaminants (Ref. 11.6). However, regeneration of AC media used for the removal of arsenic from water might not be feasible (Ref. 11.4).

The arsenic might not volatilize at the temperatures typically used in AC regeneration. In addition, off-gas containing arsenic from the regeneration process may be difficult or expensive to manage.

The reported adsorption capacity of AC is 0.020 grams of As(V) per gram of AC. As(III) is not effectively removed by AC. AC impregnated with metals such as copper and ferrous iron has a higher reported adsorption capacity for arsenic. The reported adsorption capacity for As(III) is 0.048 grams per gram of copper impregnated carbon and for As(V) is 0.2 grams per gram of ferrous iron-impregnated carbon (Ref. 11.4).

Iron-based adsorption media include granular ferric hydroxide, ferric hydroxide-coated newspaper pulp, ferric oxide, iron oxide-coated sand, sulfur-modified iron, and iron filings mixed with sand. These media have been used primarily to remove arsenic from drinking water. Processes that use these media typically remove arsenic using adsorption in combination with oxidation, precipitation/coprecipitation, ion exchange, or filtration.

For example, iron oxide-coated sand uses adsorption and ion exchange with surface hydroxides to selectively remove arsenic from water.

The media requires periodic regeneration or disposal and replacement with new media. The regeneration process is similar to that used for AA, and consists of rinsing the media with a regenerating solution containing excess sodium hydroxide, flushing with water, and neutralizing with a strong acid, such as sulfuric acid (Ref. 11.3).

The sources used for this report contained information on the use of surfactant-modified zeolite (**SMZ**) at bench scale, but no pilot- or full-scale applications were identified. SMZ is prepared by treating zeolite with a solution of surfactant, such as hexadecyltrimethylammonium bromide (**HDTMA-Br**).

This process forms a stable coating on the zeolite surface. The reported adsorption capacity of SMZ is 0.0055 grams of As(V) per gram of SMZ at 250C. SMZ must be periodically regenerated with surfactant solution or disposed and replaced with new SMZ (Ref. 11.17).

Zeolite

The name zeolite is a general term for a stonelike material which consist of crystalline metal-alumo-silicates with a large internal surface area of up to 1000 m²/g, strong electrostatic fields in the crystal lattice and with a volumetric density of about 0.8 kg/dm³.

The word zeolite is of Greek origin and means – directly translated – “**boiling rock**” which describes the effect which is to be seen if water is poured over dry zeolite. In 1925 the process of water and methanol separation using zeolites was observed for the first time. And due to this separation action (sieve action) the name “**molecular sieve**” was later attributed to zeolites.

Zeolites are non-poisonous, inflammable, are naturally available in abundance and are therefore compatible with the environment. More than 40 natural and 100 synthetic zeolites are known. The most important property of a number of zeolites is their ability for reversible adsorption of water. Even after several thousand adsorption/desorption cycles, the structural changes of the crystal lattice are insignificant if the process parameters pressure and temperature do not exceed certain limits. The application diversity of zeolites is tremendous: they are applied as molecular sieves, as adsorbents, as catalysts in cracking of hydrocarbons in the petro-chemical industry, as filler components in paper production and as ion exchange material in detergents.

Currently the chemical industry produces more than 1.4 million tons of synthetic zeolite annually and it can be expected that the world wide demand (and consequently the production) will further increase. The price, e.g. for laundry detergent zeolite is between 1.00 and 8.00 DM/kg, depending on the type and consistency of material delivered. The price for specialized zeolites is higher.



Zeolite Structures

The basic building blocks of zeolites are tetrahedral consisting of four oxygen anions and one centrally positioned silicon or aluminum cation. Zeolites are classified according to the various tetrahedral frameworks formed by these basic building blocks. The structure of the synthetic zeolites of types A, X and Y which have gained importance in industrial processes, are shown in the figure.



Structure of A-Zeolite

The aluminum and silicon atoms are positioned at the junctions while the oxygen atoms form the bridges between the tetrahedral. The difference in electro-chemical charges between the aluminum and silicon atoms per one aluminum atom results in a non-compensated negative charge. The balance is restored by metal cations which occupy preferred positions.

Because of the strong local electrical dipole movement in the lattice framework, zeolites adsorb all polar and non-polar molecules that will fit into their specific framework. This adsorption process is accompanied by release of heat-the “**heat of adsorption**”. Theoretical and experimental studies have determined quantitative heat of adsorption values for zeolite based thermal processes.

Media and Contaminants Treated

Adsorption is frequently used to remove organic contaminants and metals from industrial wastewater. It has been used to remove arsenic from groundwater and drinking water.

Summary of Performance Data

Adsorption treatment effectiveness can be evaluated by comparing influent and effluent contaminant concentrations.

Factors Affecting Adsorption Performance

- Fouling - The presence of suspended solids, organics, solids, silica, or mica, can cause fouling of adsorption media (Ref. 11.1, 11.4).
- Arsenic oxidation state - Adsorption is more effective in removing As(V) than As(III) (Ref. 11.12).
- Flow rate - Increasing the rate of flow through the adsorption unit can decrease the adsorption of contaminants (Ref. 11.1).
- Wastewater pH - The optimal pH to maximize adsorption of arsenic by activated alumina is acidic (pH 6).

Therefore, pretreatment and post-treatment of the water could be required (Ref. 11.4) achieved in both of the projects. In the other two groundwater and surface water projects the influent arsenic concentration was between 0.010 mg/L and 0.050 mg/L, and the effluent concentration was less than 0.010 mg/L.

Of the ten drinking water projects (eight full and two pilot scale) having both influent and effluent arsenic concentration data, eight had influent concentrations greater than 0.050 mg/L. Effluent concentrations of less than 0.050 mg/L were achieved in seven of these

projects. For two drinking water projects the influent arsenic concentration was between 0.010 mg/L and 0.050 mg/L, and the effluent concentration was less than 0.010 mg/L.

Projects that did not reduce arsenic concentrations to below 0.050 or 0.010 mg/L do not necessarily indicate that adsorption cannot achieve these levels. The treatment goal for some applications may have been above these levels and the technology may have been designed and operated to meet a higher arsenic concentration.

Information on treatment goals was not collected for this course.

Pilot-scale Studies

Two pilot-scale studies were performed to compare the effectiveness of AA adsorption on As(III) and As(V).

For As(III), 300 bed volumes were treated before arsenic concentrations in the effluent exceeded 0.050 mg/L, whereas 23,400 bed volumes were treated for As(V) before reaching the same concentration in the effluent. The results of these studies indicate that the adsorption capacity of AA is much greater for As(V).

The case study at the end of this section discusses in greater detail the use of AA to remove arsenic from drinking water.

Applicability, Advantages, and Potential Limitations

For AA adsorption media, the spent regenerating solution might contain a high concentration of arsenic and other sorbed contaminants, and can be corrosive (Ref. 11.3).

Spent AA is produced when the AA can no longer be regenerated (Ref. 11.3). The spent AA may require treatment prior to disposal (Ref. 11.4).

Because regeneration of AA requires the use of strong acids and bases, some of the AA media becomes dissolved during the regeneration process. This can reduce the adsorptive capacity of the AA and cause the AA packing to become "**cemented**."

Regeneration of AC media involves the use of thermal energy, which could release volatile arsenic compounds. Use of air pollution control equipment may be necessary to remove arsenic from the off-gas produced (Ref. 11.6).

Competition for adsorption sites could reduce the effectiveness of adsorption because other constituents may be preferentially adsorbed, resulting in a need for more frequent bed regeneration or replacement. The presence of sulfate, chloride, and organic compounds has reportedly reduced the adsorption capacity of AA for arsenic (Ref. 11.3).

The order for adsorption preference for AA is provided below, with the constituents with the greatest adsorption (Ref. 11.3):

OH- > H₂AsO₄- > Si(OH)₃O- > F- > HSeO₃- > SO₄²⁻ > H₃AsO₃

This technology's effectiveness is also sensitive to a variety of contaminants and characteristics in the untreated water, and suspended solids, organics, silica, or mica can cause fouling.

Therefore, it is typically applied to groundwater and drinking water, which are less likely to contain fouling contaminants. It may also be used as a polishing step for other water treatment technologies.

More detailed information on selection and design of arsenic treatment systems for small drinking water systems is available in the document "**Arsenic Treatment Technology Design Manual for Small Systems**" (Ref. 11.20).

Summary of Cost Data

One source reported that the cost of removing arsenic from drinking water using AA ranged from \$0.003 to \$0.76 per 1,000 gallons (Ref. 11.4, cost year not provided).

Factors Affecting Adsorption Costs

- Contaminant concentration - Very high concentrations of competing contaminants may require frequent replacement or regeneration of adsorbent (Ref. 11.2). The capacity of the adsorption media increases with increasing contaminant concentration (Ref. 11.1, 11.4).
- High arsenic concentrations can exhaust the adsorption media quickly, resulting in the need for frequent regeneration or replacement.
- Spent media - Spent media that can no longer be regenerated might require treatment or disposal (Ref. 11.4).

Case Study:

Treatment of Drinking Water by an Activated Alumina Plant

A drinking water treatment plant using AA installed in February 1996 has an average flow rate of 3,000 gallons per day.

The arsenic treatment system consists of two parallel treatment trains, with two AA columns in series in each train. For each of the trains, the AA media in one column is exhausted and replaced every 1 to 1.5 years after treating approximately 5,260 bed volumes.

Water samples for a long-term evaluation were collected weekly for a year. Pretreatment arsenic concentrations at the inlet ranged from 0.053 to 0.087 mg/L with an average of 0.063 mg/L. The untreated water contained primarily As(V) with only minor concentrations of As(III) and particulate arsenic. During the entire study, the arsenic concentration in the treated drinking water was below 0.003 mg/L.

Spent AA from the system had leachable arsenic concentrations of less than 0.05 mg/L, as measured by the TCLP, and therefore, could be disposed of as nonhazardous waste.

The document "**Technologies and Costs for Removal of Arsenic From Drinking Water**" (Ref. 11.3) contains detailed information on the cost of adsorption systems to treat arsenic in drinking water to below the revised MCL of 0.010 mg/L.

The document includes capital and operating and maintenance (O&M) cost curves for four adsorption processes:

- AA (at various influent pH levels)

- Granular ferric hydroxide
- Greensand filtration (KMNO₄ coated sand)
- AA point-of-use systems

Many of the technologies used to treat drinking water are applicable to treatment of other types of water, and may have similar costs.

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Changing the membrane filter on a RO unit.

Ion Exchange Treatment for Arsenic

Ion exchange has been used to treat groundwater and drinking water containing arsenic.

Based on the information collected to prepare this course, this technology typically can reduce arsenic concentrations to less than 0.050 mg/L and in some cases has reduced arsenic concentrations to below 0.010 mg/L. Its effectiveness is sensitive to a variety of untreated water contaminants and characteristics. It is used less frequently than precipitation/coprecipitation, and is most commonly used to treat groundwater and drinking water, or as a polishing step for other water treatment processes.

Technology Description: Ion exchange is a physical/chemical process in which ions held electrostatically on the surface of a solid are exchanged for ions of similar charge in a solution.

It removes ions from the aqueous phase by the exchange of cations or anions between the contaminants and the exchange medium (Ref. 12.1, 12.4, 12.8).

Media

Treated:

- Groundwater
- Surface water
- Drinking water

Exchange Media Used in Ion Exchange to Treat Arsenic:

- Strong base anion exchange resins



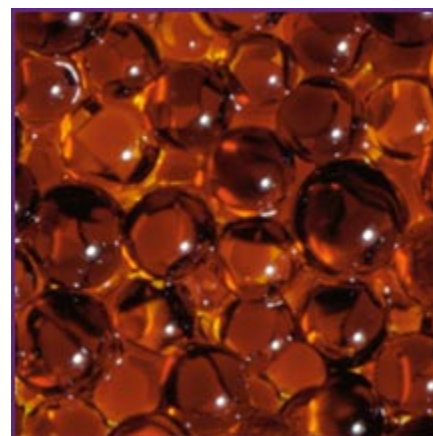
Technology Description and Principles

The medium used for ion exchange is typically a resin made from synthetic organic materials, inorganic materials, or natural polymeric materials that contain ionic functional groups to which exchangeable ions are attached (Ref. 12.3). Four types of ion exchange media have been used (Ref. 12.1):

- Strong acid
- Weak acid
- Strong base
- Weak base

Strong and weak acid resins exchange cations while strong and weak base resins exchange anions. Because dissolved arsenic is usually in an anionic form, and weak base resins tend to be effective over a smaller pH range, strong base resins are typically used for arsenic treatment (Ref. 12.1).

Resins may also be categorized by the ion that is exchanged with the one in solution.



For example, resins that exchange a chloride ion are referred to as chloride-form resins. Another way of categorizing resins is by the type of ion in solution that the resin preferentially exchanges. For example, resins that preferentially exchange sulfate ions are referred to as

sulfate-selective. Both sulfate-selective and nitrate-selective resins have been used for arsenic removal (Ref. 12.1).

The resin is usually packed into a column, and as contaminated water is passed through the column, contaminant ions are exchanged for other ions such as chloride or hydroxide in the resin (Ref. 12.4). Ion exchange is often preceded by treatments such as filtration and oil-water separation to remove organics, suspended solids, and other contaminants that can foul the resins and reduce their effectiveness.

Ion exchange resins must be periodically regenerated to remove the adsorbed contaminants and replenish the exchanged ions (Ref. 12.4).

Regeneration of a resin occurs in three steps:

- Backwashing
- Regeneration with a solution of ions
- Final rinsing to remove the regenerating solution

The regeneration process results in a backwash solution, a waste regenerating solution, and a waste rinse water. The volume of spent regeneration solution ranges from 1.5 to 10 percent of the treated water volume depending on the feed water quality and type of ion exchange unit (Ref. 12.4). The number of ion exchange bed volumes that can be treated before regeneration is needed can range from 300 to 60,000 (Ref. 12.1).

The regenerating solution may be used up to 25 times before treatment or disposal is required.

Factors Affecting Ion Exchange Performance

- **Valence state** - As(III) is generally not removed by ion exchange (Ref. 12.4).
- **Presence of competing ions** - Competition for the exchange ion can reduce the effectiveness of ion exchange if ions in the resin are replaced by ions other than arsenic, resulting in a need for more frequent bed regeneration (Ref. 12.1, 12.9).
- **Fouling** - The presence of organics, suspended solids, calcium, or iron, can cause fouling of ion exchange resins (Ref. 12.4).
- **Presence of trivalent iron** - The presence of Fe (III) could cause arsenic to form complexes with the iron that are not removed by ion exchange (Ref. 12.1).
- **pH** - For chloride-form, strong-base resins and a pH in the range of 6.5 to 9 is optimal. Outside of this range, arsenic removal effectiveness decreases quickly (Ref. 12.1).

Final Rinsing Step

The final rinsing step usually requires only a few bed volumes of water (Ref. 12.4).

Ion exchange can be operated using multiple beds in series to reduce the need for bed regeneration; beds first in the series will require regeneration first, and fresh beds can be added at the end of the series. Multiple beds can also allow for continuous operation because some of the beds can be regenerated while others continue to treat water. Ion exchange beds are typically operated as a fixed bed, in which the water to be treated is passed over an immobile ion exchange resin.

One variation on this approach is to operate the bed in a nonfixed, countercurrent fashion in which water is applied in one direction, usually downward, while spent ion exchange resin is removed from the top of the bed.

Regenerated resin is added to the bottom of the bed. This method may reduce the frequency of resin regeneration (Ref. 12.4).

Media and Contaminants Treated

Anion exchange resins are used to remove soluble forms of arsenic from wastewater, groundwater, and drinking water (Ref. 12.1, 12.4). Ion exchange treatment is generally not applicable to soil and waste.

It is commonly used in drinking water treatment for softening, removal of calcium, magnesium, and other cations in exchange for sodium, as well as removing nitrate, arsenate, chromate, and selenate (Ref. 12.9).

Type, Number, and Scale of Identified Projects Treating Water Containing Arsenic

Ion exchange of arsenic and groundwater, surface water, and drinking water is commercially available.

Information is available on seven full-scale applications, including three applications to groundwater and surface water, and four applications to drinking water. No pilot-scale applications or applications to industrial wastewater were found in the sources researched.

Summary of Performance Data

Ion exchange treatment effectiveness can be evaluated by comparing influent and effluent contaminant concentrations. The single surface water project with both influent and effluent arsenic concentration data had an influent concentration of 0.0394 mg/L, and an effluent concentration of 0.0229 mg/L.

Of the three drinking water projects with both influent and effluent concentration data, all had influent concentrations greater than 0.010 mg/L. Effluent concentrations of less than 0.010 mg/L were consistently achieved in only one of these projects.

Projects that did not reduce arsenic concentrations to below 0.050 or 0.010 mg/L do not necessarily indicate that ion exchange cannot achieve these levels. The treatment goal for some applications could have been above these levels and the technology may have been designed and operated to meet a higher arsenic concentration. Information on treatment goals was not collected for this report.

Factors Affecting Ion Exchange Costs

- **Bed regeneration** - Regenerating ion exchange beds reduces the amount of waste for disposal and the cost of operation (Ref. 12.1).
- **Sulfate** - Sulfate (SO₄) can compete with arsenic for ion exchange sites, thus reducing the exchange capacity of the ion exchange media for arsenic. This can result in a need for more frequent media regeneration or replacement and associated higher costs (Ref. 12.1).

Case Study:

National Risk Management Research Laboratory Study

A study by the EPA ORD's National Risk Management Research Laboratory tested an ion exchange system at a drinking water treatment plant. Weekly sampling for one year showed that the plant achieved an average of 97 percent arsenic removal.

The resin columns were frequently regenerated (every 6 days). Influent arsenic concentrations ranged from 0.045 to 0.065 mg/L and effluent concentrations ranged from 0.0008 to 0.0045 mg/L (Ref. 12.9).

The case study at the end of this section further discusses the use of ion exchange to remove arsenic from drinking water.

Applicability, Advantages, and Potential Limitations

For ion exchange systems using chloride-form resins, the treated water could contain increased levels of chloride ions and as a result be corrosive. Chlorides can also increase the redox potential of iron, thus increasing the potential for water discoloration if the iron is oxidized.

The ion exchange process can also lower the pH of treated waters (Ref. 12.4).

For ion exchange resins used to remove arsenic from water, the spent regenerating solution might contain a high concentration of arsenic and other sorbed contaminants, and could be corrosive. Spent resin is produced when the resin can no longer be regenerated.

The spent resin may require treatment prior to reuse or disposal (Ref. 12.8).

The effectiveness of ion exchange is also sensitive to a variety of contaminants and characteristics in the untreated water, and organics, suspended solids, calcium, or iron can cause fouling. Therefore, it is typically applied to groundwater and drinking water, which are less likely to contain fouling contaminants. It may also be used as a polishing step for other water treatment technologies.

More detailed information on selection and design of arsenic treatment systems for small drinking water systems is available in the document "**Arsenic Treatment Technology Design Manual for Small Systems**" (Ref. 12.10).

Summary of Cost Data

One project reported a capital cost for an ion exchange system of \$6,886 with an additional \$2,000 installation fee (Ref. 12.9, cost year not provided). The capacity of the system and O&M costs were not reported. Cost data for other projects using ion exchange were not found.

The document "**Technologies and Costs for Removal of Arsenic From Drinking Water**" (Ref. 12.1) contains additional information on the cost of ion exchange systems to treat arsenic in drinking water to levels below the revised MCL of 0.010 mg/L. The document includes capital and O&M cost curves for ion exchange at various influent sulfate (SO₄) concentrations.

These cost curves are based on computer cost models for drinking water treatment systems. The curves estimate the costs for ion exchange treatment systems with different design flow rates. The document also contains information on the disposal cost for residuals from ion exchange. Many of the technologies used to treat drinking water are applicable to treatment of other types of water, and may have similar costs.

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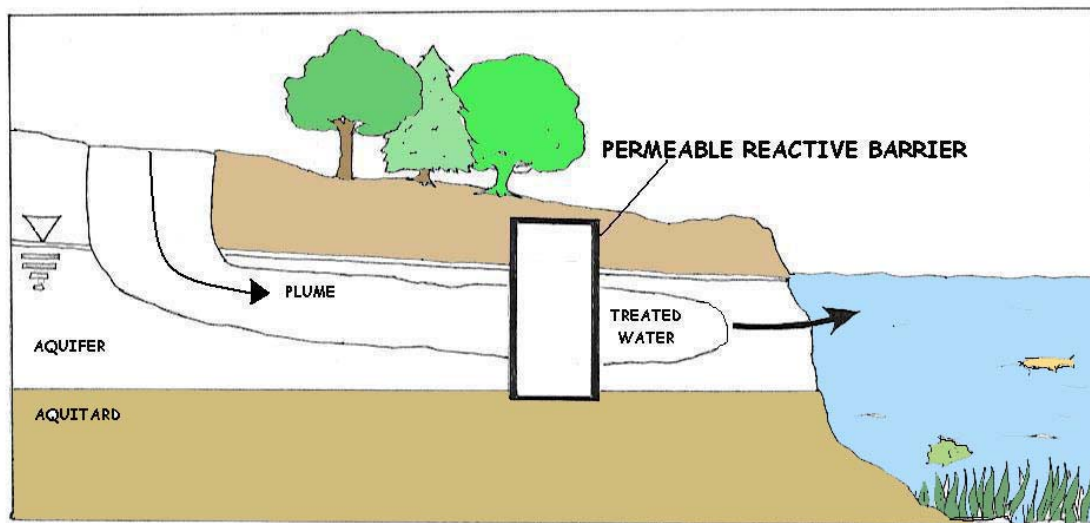


It is known that even if your water has detectable levels of arsenic that are below the 0.010 mg/L MCL, and you have iron pipes or components in your distribution system, your system's pipes may have arsenic-rich scales attached to them. As long as the scales are not disturbed, they will remain attached to the pipes or other distribution system components. Certain conditions, such as flushing of mains or fire flow conditions, may result in those scales being sloughed off and suspended in the water, releasing the arsenic. Other conditions, such as changes in water chemistry, may result in some of the arsenic dissolving back into the water. Both of these situations could cause high arsenic levels at consumers' taps.

Permeable Reactive Barriers for Arsenic

Permeable reactive barriers (**PRBs**) are being used to treat arsenic in groundwater at full scale at only a few sites. Although many candidate materials for the reactive portion of the barrier have been tested at bench scale, only zero valent iron and limestone have been used at full scale.

The installation techniques for PRBs are established for depths less than 30 feet, and require innovative installation techniques for deeper installations.



Technology Description and Principles

PRBs are applicable to the treatment of both organic and inorganic contaminants. The former usually are broken down into carbon dioxide and water, while the latter are converted to species that are less toxic or less mobile.

The most frequent applications of PRBs is the in situ treatment of groundwater contaminated with chlorinated solvents. A number of different treatment media have been used, the most common being zero valent iron (**ZVI**). Other media include hydrated lime, slag from steelmaking processes that use a basic oxygen furnace, calcium oxides, chelators (ligands selected for their specificity for a given metal), iron oxides, sorbents, substitution agents (e.g., ion exchange resins) and microbes (Ref. 13.6, 13.8, 13. 18).

The cost of the reactive media will impact the overall cost of PRB remedies. The information sources used for this report included information about PRB applications using ZVI, basic oxygen furnace slag, limestone, surfactant modified zeolite, and ion exchange resin to treat arsenic.

Technology Description: Permeable reactive barriers (**PRBs**) are walls containing reactive media that are installed across the path of a contaminated groundwater plume to intercept the plume. The barrier allows water to pass through while the media remove the contaminants by precipitation, degradation, adsorption, or ion exchange.

Media Treated:

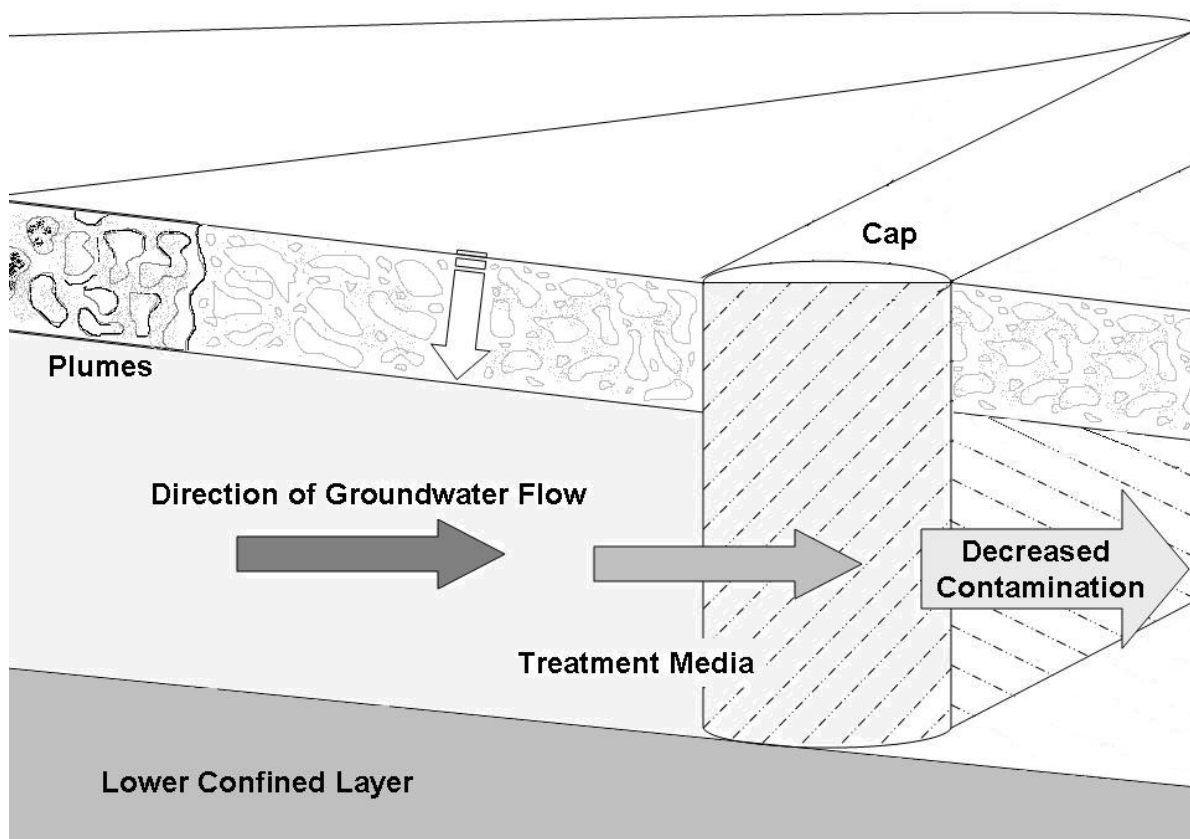
- Groundwater (in situ)

Chemicals and Reactive Media Used in PRBs to Treat Arsenic:

- Zero valent iron (ZVI)
- Limestone
- Basic oxygen furnace slag
- Surfactant modified zeolite
- Ion exchange resin

Installation Depth:

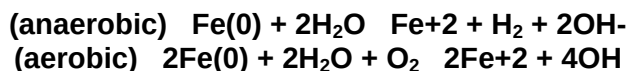
- Up to 30 feet deep using established techniques
- Innovative techniques required for depths greater than 30 feet



For the PRB projects identified for this course, ZVI was the most commonly used reactive media. As groundwater reacts with ZVI, pH increases, Eh decreases, and the concentration of dissolved hydrogen increases. These basic chemical changes promote a variety of processes that impact contaminant concentrations. Increases in pH favor the precipitation of carbonates of calcium and iron as well as insoluble metal hydroxides. Decreases in Eh drive reduction of metals and metalloids with multiple oxidation states.

Finally, an increase in the partial pressure of hydrogen in subsurface systems supports the activity of various chemotrophic organisms that use hydrogen as an energy source, especially sulfate-reducing bacteria and iron-reducing bacteria (Ref. 13.15).

Arsenate [As (V)] ions bind tightly to the iron filings, causing the ZVI to be oxidized to ferrous iron, aerobically or anaerobically in the presence of water, as shown by the following reactions:



The process results in a positively charged iron surface that sorbs the arsenate species by electrostatic interactions (Ref. 13.5, 13.17). In systems where dissolved sulfate is reduced to sulfide by sulfate-reducing bacteria, arsenic may be removed by the precipitation of insoluble arsenic sulfide (As_2S_3) or co-precipitated with iron sulfides (FeS) (Ref. 13.15). PRBs can be constructed by excavating a trench of the appropriate width and backfilling it with a reactive medium.

Commercial PRBs are built in two basic configurations: the funnel-and-gate and the continuous wall. The funnel-and-gate uses impermeable walls, for example, sheet pilings or slurry walls, as a “**funnel**” to direct the contaminant plume to a “**gate(s)**” containing the reactive media, while the continuous wall transects the flow path of the plume with reactive media (Ref. 13.6). Most PRBs installed to date have had depths of 50 feet (ft) or less. Those having depths of 30 ft or less can be installed with a continuous trencher, while depths between 30 and 70 ft require a more innovative installation method, such as biopolymers. Installation of PRBs at depths greater than 70 ft is more challenging (Ref. 13.13).

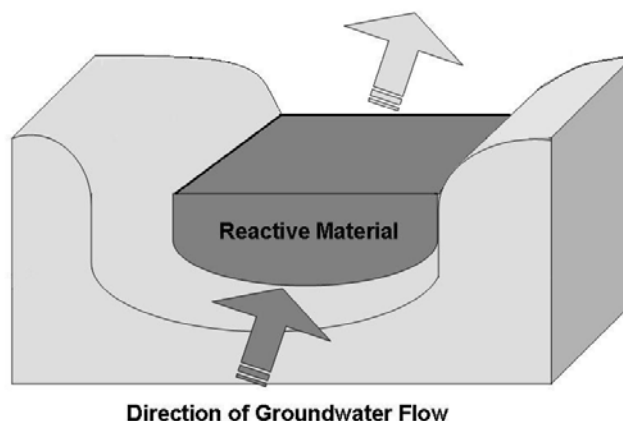
Media and Contaminants Treated

This technology can treat both organic and inorganic contaminants. Organic contaminants are broken down into less toxic elements and compounds, such as carbon dioxide and water. Inorganic contaminants are converted to species that are less toxic or less mobile.

Inorganic contaminants that can be treated by PRBs include, but are not limited to, chromium (Cr), nickel (Ni), lead (Pb), uranium (U), technetium (Tc), iron (Fe), manganese (Mn), selenium (Se), cobalt (Co), copper (Cu), cadmium (Cd), zinc (Zn), arsenic (As), nitrate (NO_3^-), sulfate (SO_4^{2-}), and phosphate (PO_4^{3-}).

The characteristics that these elements have in common is that they can undergo redox reactions and can form solid precipitates with common groundwater constituents, such as carbonate (CO_3^{2-}), sulfide (S^{2-}), and hydroxide (OH^-). Some common sources of these contaminants are mine tailings, septic systems, and battery recycling/disposal facilities (Ref. 13.5, 13.6, 13.14). PRBs are designed to treat groundwater in situ. This technology is not applicable to other contaminated media such as soil, debris, or industrial wastes.

Permeable Reactive Barrier Installation



Type, Number, and Scale of Identified Projects Treating Water Containing Arsenic

PRBs are commercially available and are being used to treat groundwater containing arsenic at a full scale at two Superfund sites, the Monticello Mill Tailings and Tonolli Corporation sites, although arsenic is not the primary target contaminant for treatment by the technology at either site (Ref. 13.1). At a third Superfund site, the Asarco East Helena site, this technology has been tested at a bench scale, and implementation at a full scale to treat arsenic is currently planned (Ref. 13.15). In 1999, a pilot-scale treatment was conducted at Bodo Canyon Disposal Cell Mill Tailings Site, Durango, Colorado, to remediate groundwater contaminated with arsenic (Ref. 13.12).

In addition, PRBs have been used in two bench-scale treatability studies by the U.S. Department of Energy's Grand Junction Office (GJO) to evaluate their application to the Monticello Mill Tailings site and a former uranium ore processing site (Ref. 13.3). Additional bench-scale studies of the treatment of arsenic using PRBs that contain various reactive media are listed below (Ref. 13.8, 13.11). These studies were not conducted to evaluate the application of PRBs to specific sites.

Factors Affecting PRB Performance

Fractured rock - The presence of fractured rock in contact with the PRB may allow groundwater to flow around, rather than through, the PRB (Ref. 13.6).

Deep aquifers and contaminant plumes - PRBs may be difficult to install for deep aquifers and contaminant plumes (>70 ft deep) (Ref. 13.13).

High aquifer hydraulic conductivity - The hydraulic conductivity of the barrier must be greater than that of the aquifer to prevent preferential flow around the barrier (Ref. 13.13).

Stratigraphy - Site stratigraphy may affect PRB installation. For example, clay layers might be "*smear*ed" during installation, reducing hydraulic conductivity near the PRB (Ref. 13.6).

Barrier plugging - Permeability and reactivity of the barrier may be reduced by precipitation products and microbial growth (Ref. 13.6).

Other Bench-Scale Studies Using Adsorption or Ion Exchange Barriers

- . Activated alumina (Dupont)
- . Bauxite (Dupont)
- . Ferric oxides and oxyhydroxides (Dupont, University of Waterloo),
- . Peat, humate, lignite, coal (Dupont)
- . Surfactant-modified zeolite (New Mexico Institute of Mining and Technology)

Other Bench-Scale Studies Using Precipitation Barriers

- . Ferrous hydroxide, ferrous carbonate, ferrous sulfide (Dupont)
- . Limestone (Dupont)
- . Zero-Valent Metals (DOE GJO)

Applicability, Advantages, and Potential Limitations

PRBs are a passive treatment technology, designed to function for a long time with little or no energy input. They produce less waste than active remediation (for example, extraction systems like pump and treat), as the contaminants are immobilized or altered in the subsurface (Ref. 13.14). PRBs can treat groundwater with multiple contaminants and can be effective over a range of concentrations. PRBs require no above-ground equipment, except monitoring devices, allowing return of the property to economic use during remediation (Ref. 13.5, 13.14).

PRBs are best applied to shallow, unconfined aquifer systems in unconsolidated deposits, as long as the reactive material is more conductive than the aquifer. (Ref. 13.13). PRBs rely on the natural movement of groundwater; therefore, aquifers with low hydraulic conductivity can require relatively long periods of time to be remediated. In addition, PRBs do not remediate the entire plume, but only the portion of the plume that has passed through the PRB. Because cleanup of groundwater contaminated with arsenic has been conducted at only two Superfund sites and these barriers have been recently installed (Tonolli in 1998 and Monticello in 1999), the long-term effectiveness of PRBs for arsenic treatment has not been demonstrated (Ref. 13.13).

Case Study: Monticello Mill Tailings Site

Permeable Reactive Barrier

The Monticello Mill Tailings in Southeastern Utah is a former uranium/vanadium processing mill and mill tailings impoundment (disposal pit). In January 1998, the U.S. Department of Energy completed an interim investigation to determine the nature and extent of contamination in the surface water and groundwater in operable unit 3 of the site.

Arsenic was one of several contaminants in the groundwater, and was found at concentrations ranging from 0.010 to 0.013 mg/L. A PRB containing ZVI was constructed in June 1999 to treat heavy metal and metalloid contaminants in the groundwater. Five rounds of groundwater sampling occurred between June 1999 and April 2000, and sampling was expected to continue on a quarterly basis until July 2001. The average concentration of arsenic entering the PRB, as measured from September to November 1999 was 0.010 mg/L, and the effluent concentration, measured in April 2000, was less than 0.0002 mg/L (Ref. 13.1, 13.2, 13.14)

Factors Affecting PRB Costs

PRB depth - PRBs at depths greater than 30 feet may be more expensive to install, requiring special excavation equipment and construction materials (Ref. 13.13).

Reactive media - Reactive media vary in cost, therefore the reactive media selected can affect PRB cost.

Summary of Cost Data

The EPA compared the costs of pump-and-treat systems at 32 sites to the costs of PRBs at 16 sites. Although the sites selected were not a statistically representative sample of groundwater remediation projects, the capital costs for PRBs were generally lower than those for pump and treat systems (Ref. 13.13).

However, at the Monticello site, estimates showed that capital costs for a PRB were greater than those for a pump-and-treat system, but lower operations and maintenance costs would result in a lower life-cycle cost to achieve similar cleanup goals. For the PRB at the Monticello site, total capital cost was \$1,196,000, comprised of \$1,052,000 for construction and \$144,000 for the reactive PRB media. Construction costs are assumed to include actual construction costs and not design activities or treatability studies (Ref. 13.14, cost year not provided). Cost data for the other projects described in this section are not available.

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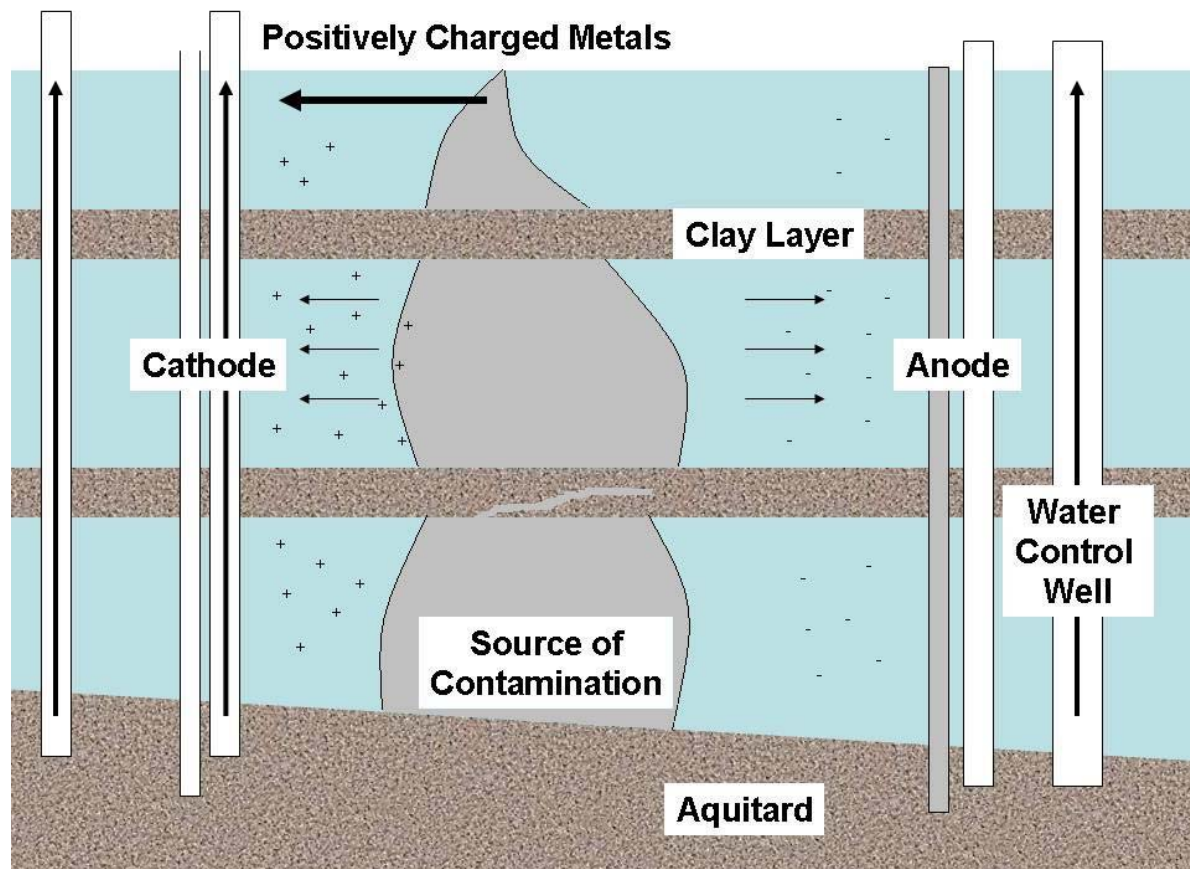
Electrokinetic Treatment of Arsenic

Electrokinetic treatment is an emerging remediation technology designed to remove heavy metal contaminants from soil and groundwater. The technology is most applicable to soil with small particle sizes, such as clay.

However, its effectiveness may be limited by a variety of contaminants and soil and water characteristics.

Information sources researched for this report identified a limited number of applications of the technology to arsenic.

Technology Description: Electrokinetic remediation is based on the theory that a low-density current will mobilize contaminants in the form of charged species. A current passed between electrodes is intended to cause water, ions, and particulates to move through the soil, waste, and water (Ref. 14.8). Contaminants arriving at the electrodes can be removed by means of electroplating or electrodeposition, precipitation or coprecipitation, adsorption, complexing with ion exchange resins, or by pumping of water (or other fluid) near the electrode (Ref. 14.10).



Electrokinetics to Remediate Water Soluble Metals

Electrical Current - Electrical resistance heating and electrokinetics can move metals, mobilize Non Aqueous Phase Liquids (NAPLS), or heat the soil as high as 250 °F to vaporize NAPLS. Both technologies work because moist soil conducts electric current.

Thus, it can either be heated, and vaporized NAPLS can be collected at wells or electrodes, or ions can move with the current and be collected at other types of electrodes.

The resistance of the soil and mobility of fluids are controlled by the soil moisture, so this must be controlled, sometimes by injecting water.

The wells must be closely spaced, so capital cost for a project is higher. While heating is a fast process, moving ions with a current is much slower since the current must change the charge on the soil in order to mobilize ions.

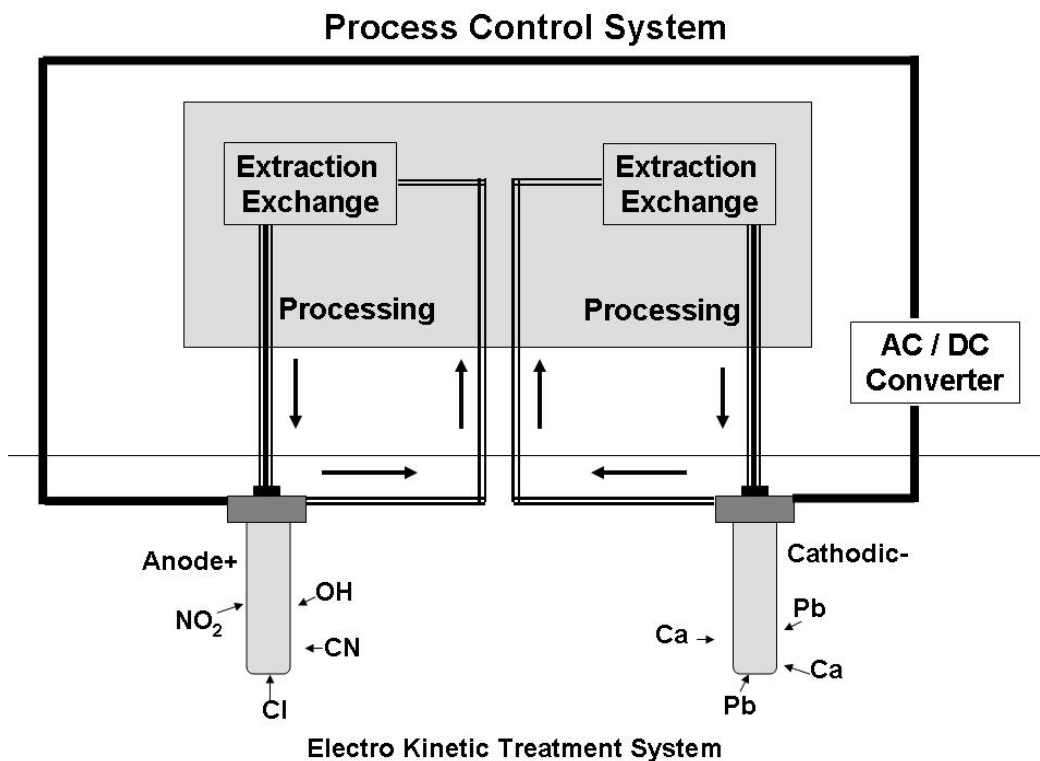
However, electrokinetics is one of the few technologies for recovering metals, and resistance heating works well in clay layers.

Media Treated:

- Soil
- Groundwater
- Industrial wastes

Chemicals Used in Electrokinetic Process to Treat Arsenic:

- Sulfuric Acid
- Phosphoric Acid
- Oxalic Acid



Technology Description and Principles

In situ electrokinetic treatment of arsenic uses the natural conductivity of the soil (created by pore water and dissolved salts) to affect movement of water, ions, and particulates through the soil (Ref. 14.8). Water and/or chemical solutions can also be added to enhance the recovery of metals by electrokinetics.

Factors Affecting Electrokinetic Treatment Performance

- **Contaminant properties** - The applicability of electrokinetics to soil and water containing arsenic depends on the solubility of the particular arsenic species.

Electrokinetic treatment is applicable to acid-soluble polar compounds, but not to insoluble metals (Ref. 14.6).

- **Salinity and cation exchange capacity** – The technology is most efficient when these parameters are low (Ref. 14.14). Chemical reduction of chloride ions at the anode by the electrokinetic process may also produce chlorine gas (Ref. 14.6).

- **Soil moisture** - Electrokinetic treatment requires adequate soil moisture; therefore addition of a conducting pore fluid may be required (Ref. 14.7). Electrokinetic treatment is most applicable to saturated soils (Ref. 14.9). However, adding fluid to allow treatment of soils without sufficient moisture may flush contaminants out of the targeted treatment area.

- **Polarity and magnitude of the ionic charge** - These factors affect the direction and rate of contaminant movement (Ref. 14.11).

- **Soil type** - Electrokinetic treatment is most applicable to homogenous soils (Ref. 14.9). Fine-grained soils are more amenable to electrokinetic treatment due to their large surface area, which provides numerous sites for reactions necessary for electrokinetic processes (Ref. 14.13).

- **pH** - The pH can affect process electrochemistry and cause precipitation of contaminants or other species, reducing soil permeability and inhibiting recovery. The deposition of precipitation solids may be prevented by flushing the cathode with water or a dilute acid (Ref. 14.14).

This technology can also be applied ex situ to groundwater by passing the water between electrodes. The current causes arsenic to migrate toward the electrodes, and also alters the pH and oxidation-reduction potential of the water, causing arsenic to precipitate/ coprecipitate. The solids are then removed from the water using clarification and filtration (Ref.14.21).

Media and Contaminants Treated

Electrokinetic treatment is an in situ treatment process that has had limited use to treat soil, groundwater, and industrial wastes containing arsenic. It has also been used to treat other heavy metals such as zinc, cadmium, mercury, chromium, and copper (Ref. 14.1, 14.4, 14.20).

Electrokinetic treatment may be capable of removing contaminants from both saturated and unsaturated soil zones, and may be able to perform without the addition of chemical or biological agents to the site. This technology also may be applicable to low-permeability soils, such as clay (Ref. 14.1, 14.4, 14.9).

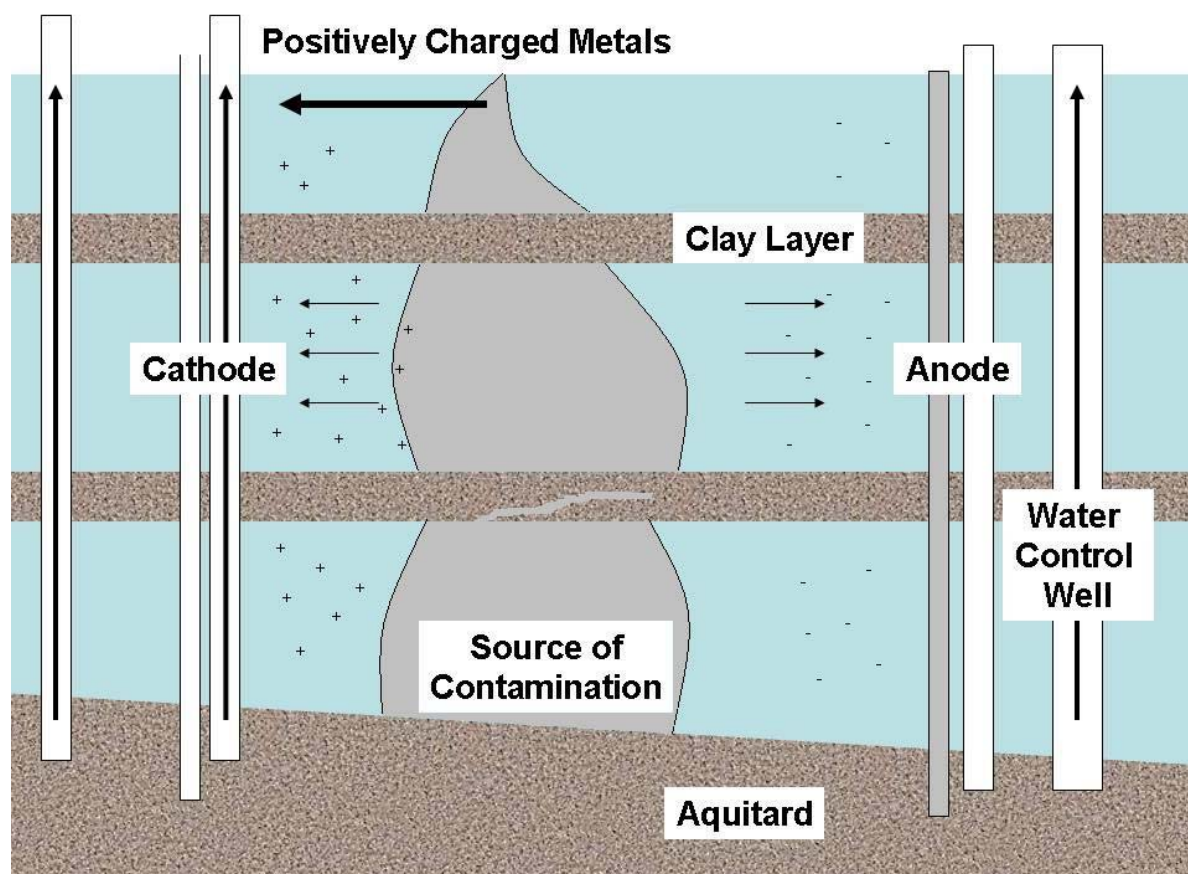


Applicability, Advantages, and Potential Limitations

Electrokinetics is an emerging technology with relatively few applications for arsenic treatment. It is an in situ treatment technology, and therefore does not require excavation of contaminated soil or pumping of contaminated groundwater. Its effectiveness may be limited by a variety of soil and contaminant characteristics.

Charged metal or metalloid cations, such as As (V) and As (III) migrate to the negatively-charged electrode (cathode), while metal or metalloid anions migrate to the positively charged electrode (anode) (Ref. 14.9).

Extraction may occur at the electrodes or in an external fluid cycling/extraction system (Ref. 14.11). Alternately, the metals can be stabilized in situ by injecting stabilizing agents that react with and immobilize the contaminants (Ref. 14.12). Arsenic has been removed from soils treated by electrokinetics using an external fluid cycling/ extraction system (Ref. 14.2, 14.18).



Case Study: The Overpelt Project

A pilot-scale test of electrokinetic remediation of arsenic in groundwater was conducted in Belgium in 1997. This ex situ application involved pumping groundwater contaminated with zinc, arsenic, and cadmium and treating it in an electrokinetic remediation system with a capacity of 6,600 gpm.

The treatment system precipitated the contaminants, and the precipitated solids were removed using clarification and filtration. The electrokinetic treatment system did not use additives or chemicals. The treatment reduced arsenic concentrations in groundwater from 0.6 mg/L to 0.013 mg/L. The reported costs of the treatment were \$0.004 per gallon for total cost, and \$0.002 per gallon for O&M. (Ref. 14.21)

Factors Affecting Electrokinetic Treatment Costs

- **Contaminant extraction system** – Some electrokinetic systems remove the contaminant from the subsurface using an extraction fluid. In such systems, the extraction fluid may require further treatment, which can increase the cost (Ref. 14.4).

Scale of Electrokinetic Projects for Arsenic Treatment

Summary of Cost Data

Estimated costs of in situ electrokinetic treatment of soils containing arsenic range from \$50 - \$270 per cycle. (Ref. 14.2, 14.4, cost year not provided). The reported costs for one pilot-scale, ex situ treatment of groundwater of the treatment were \$0.004 per gallon for total cost, and \$0.002 per gallon for O&M. (Ref. 14.21)



In Situ Electrokinetic Remediation for Metal Contaminated Soils

Primary Contributors

Military activities are one of the primary contributors to metals contaminated soil problems. Military operations such as small arms training, electroplating and metal finishing operations, explosive and propellant manufacturing and use, and the use of lead based paint at military facilities, have resulted in vast tracts of land being contaminated with metals. As a result, there is a military need to develop cost-effective methods for cleaning up metal contaminated soils. Electrokinetic remediation was identified as a possible method of performing an in situ extraction of the metal contaminants from soils.



Electrokinetic remediation is an in-situ process in which an electrical field is created in a soil matrix by applying a low-voltage direct current (**DC**) to electrodes placed in the soil. As a result of the application of this electric field, heavy metal contaminants may be mobilized, concentrated at the electrodes, and extracted from the soil.

Many vendors have marketed the potential of electrokinetic remediation for metals contaminated soils, however, no large scale field demonstrations had been conducted. Issues such as control of contaminant movement, ability to achieve cleanup goals, byproduct formation, treatment effects on the soil matrix, etc. had not been addressed. Interest in electrokinetic remediation has been driven by the demand for technologies that are cost effective and will eliminate the long-term liability that is incurred by landfilling of contaminants.

Approach

The US Army Environmental Center (**USAEC**) and the Engineer Research and Development Center (**ERDC**) conducted a field demonstration of electrokinetic remediation to assess the performance and cost of the technology. This demonstration, sponsored by the Environmental Security Technology Certification Program and the Southwest Division, Naval Facilities Engineering Command, was conducted at a metals contaminated site at Naval Air Weapons Station (**NAWS**) Point Mugu, California.

Results

The bench tests conducted prior to field operations did not accurately reflect the effects that site conditions would have on the technology, specifically the retarding effects that competing ions would have on pH front development and contaminant mobility. Contaminant mobility and pH effects were ultimately observed in the field, however, the duration required for treatment in the field will be much longer than anticipated by the bench tests.



Also, the bench tests did not reflect the by-product formation that was encountered in the field, specifically the hydrogen sulfide gas and trihalomethane formation. As currently designed, the bench tests do not provide an adequate means of predicting performance, duration, and efficiency or the formation of potentially hazardous by-products as a result of the technology's reaction with site specific constituents. At best, it provided an indication that contaminants would ultimately be mobilized when the technology is applied.

The performance goal for the technology was to reduce contaminant levels to California State TTLC and STLC levels as well as to established Modified Region 9 Preliminary Remediation Goals. No contaminants were extracted during the demonstration period. The technology had an impact on organic contaminants at the site. An increase in organic contaminants was detected. This was primarily a result of the trihalomethane production resulting from the chlorine buildup in the anode wells. The VOC data also indicated that there was an increase in the vinyl chloride concentrations in some of the wells. The increase in the vinyl chloride concentration is attributed to acceleration of the naturally occurring dehalogenation of PCE and TCE as a result of the electrokinetic remediation system operation.

The site characteristic that most affected the treatment performance was the high chloride concentration of the groundwater. The chloride reactions at the anode act to retard the development of the pH front, which in turn lengthens the time required to extract the contaminants from the soil.

Conclusions

Electrokinetic remediation heavy metal extraction rate and efficiency is dependent upon many subsurface characteristics such as soil type and grain size, contaminant concentration, ionic mobility, total ionic concentration, types of contaminant species and their solubility, etc.

Additional complications with the application of electrokinetic remediation can arise from the presence of organic contaminants and possibly the organic material in the soil.

The soil's physical, chemical, and biological characteristics can individually and cumulatively impact the extraction rate and efficiency of the technology. As a result of the numerous factors affecting performance, the following technology application issues and performance concerns have been identified:

- There is a lack of understanding of the technology's effects on naturally occurring ions and how these effects impact mobilization and removal of the target contaminants. The field demonstration at NAWA Point Mugu identified many discrepancies between the laboratory testing and the performance observed in the field test. The retarding effects created by the naturally occurring ions cannot be accurately quantified in the laboratory tests and their effects on the type of metal species formed under the electric field influence cannot be accurately predicted. The metals species observed in the laboratory testing differed from those observed in the field. The species development will affect migration rate and extraction efficiency.
- The presence of naturally occurring ions and organic material as well as organic contaminants can result in the development of potentially hazardous by-products (i.e. chlorine, trihalomethanes, acetone, etc.) when an electric field is applied to the soil.
- The addition of ions to the soil as a result of the amendment addition to the cathode well

may also result in the formation of hazardous by-products during operation of the technology.

- Laboratory treatability testing as currently designed cannot identify the potential for by-product production.
- The ability of the electric field to control the movement of mobilized contaminant ions in treatment zones affected by groundwater flow or tidal influences has not been validated.
- The soil chemical and biological factors that may limit the application of electrokinetic remediation have yet to be adequately quantified. As a result, site screening using readily measurable soil characteristics cannot be performed. Also as previously stated, laboratory treatability testing may give a false indication of the applicability of electrokinetic remediation to a specific site.
- The impact that electrokinetic extraction will have on the soil's physical, chemical, and biological characteristics has not been addressed. Application of an electric field has not produced any measurable adverse impacts; however, changes to the soil (and their potential ecological impacts) after cleanup target levels have been reached have not been assessed.
- There is a lack of understanding of the impact that electrode shape and electrode placement will have on the electric field shape and intensity formed within the soil matrix. The electric field shape and intensity will effect the formation of and movement of mobile heavy metal species. If complete coverage of the treatment area is not achieved, then all of the contaminants may not be extracted.
- Determination of the appropriate current density to the treatment area appears to be more of an art than a science. Current density or voltage application to the treatment area cannot be correlated to any specific measurable site parameter(s). Considering that electric field intensity can affect the types of contaminant species developed as well as impact the soil's physical, chemical, and biological properties, this parameter and the effects that varying this parameter has requires investigation and quantification.
- Those marketing the technology have not accurately represented the cost of applying electrokinetic remediation for heavy metals extraction. Typically, only power and chemical costs are referred to, thus giving the impression that this is a low-cost technology. Equipment costs, installation, maintenance, removal, and contaminant disposal significantly increase the turnkey cost of applying electrokinetic remediation. Depending on the site conditions and system design, treatment costs may vary from \$150 to \$1,200 per cubic yard.

Full-scale application of this technology for remediation of metals contaminated soil is limited at best until the issues and concerns stated above can be resolved.

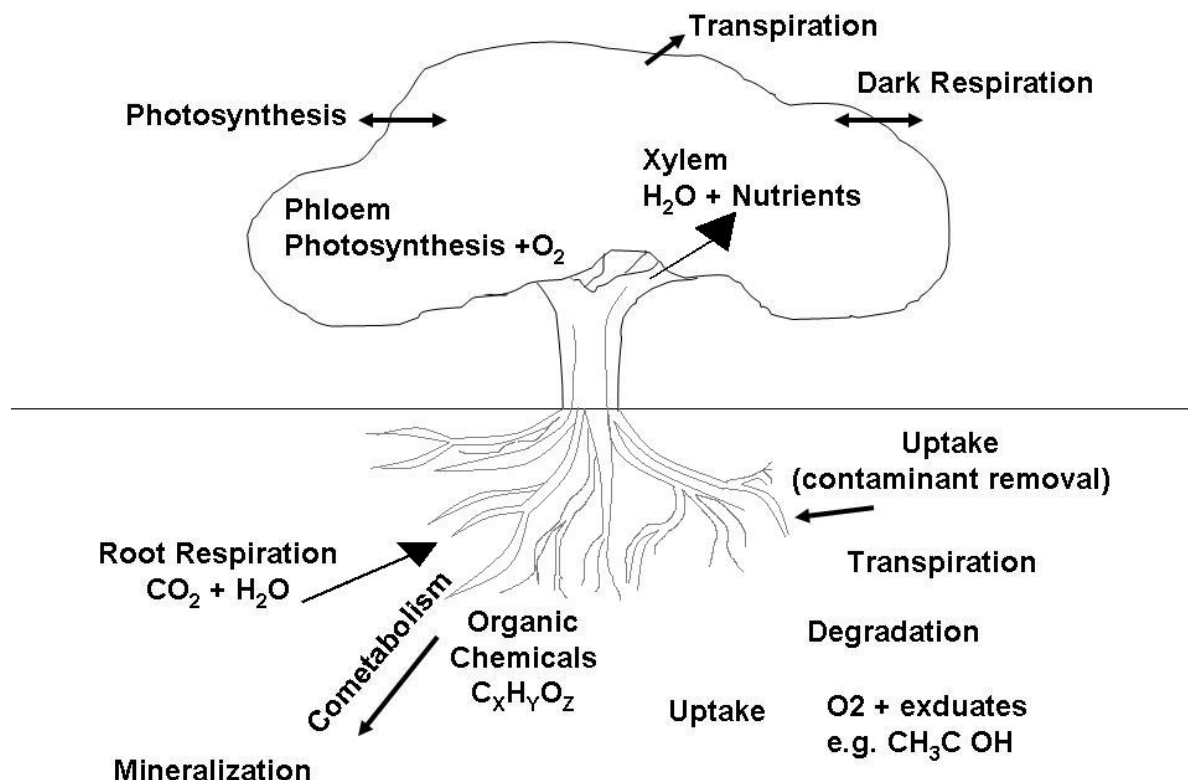
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Phytoremediation Treatment of Arsenic

Phytoremediation is an emerging technology.

What is phytoremediation?



Model of Phytoremediation

Phytoremediation is the use of plants to clean up pollution in the environment, especially at hazardous waste sites. Plants can take up and accumulate toxic metals in their leaves where they can be disposed of easily. Organic pollutants can be taken up by plants and degraded by plant metabolic activities. The action of bacteria associated with plant roots may be useful in the control of pollutants.

Research into phytoremediation has intensified since the early 1990s. Studies at the University of Washington have led the way in understanding plant activities against important toxic compounds such as trichloroethylene (number one on the Superfund list of prevalent groundwater pollutants) and carbon tetrachloride. Recently we have begun work in the use of plants to destroy toxic compounds in munitions wastes. We continue to study the mechanisms that are responsible for pollutant degradation by plants and to develop ways to increase the usefulness of plants for phytoremediation.

Applications

Phytoremediation has been applied to or proposed for cleanup of many types of hazardous wastes, including toxic metals and man-made organic compounds.

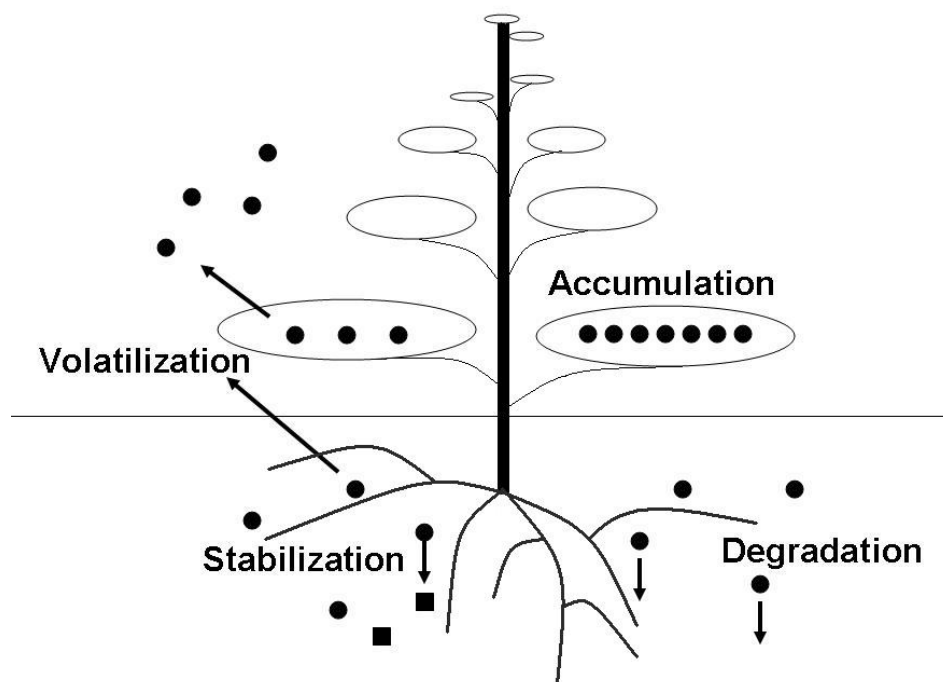
Metals

Certain plants can take up large amounts of some toxic heavy metals from the soil. For example, some trees adapted to growth on serpentine soils in the South Pacific, which are naturally high in nickel, take up the metal and concentrate it in their tissues, so much that the sap of the trees is a bright blue. This phenomenon has inspired scientists and engineers to propose to develop plants that can "**hyperaccumulate**" heavy metals in their above-ground tissues so that, by harvesting them, the metals can be economically removed in an ecologically friendly manner.

Organics

Soluble compounds

The most important and widespread of groundwater pollutants are the chlorinated hydrocarbons, such as trichloroethylene. Plants can take up these carcinogens and break them down to harmless products such as chloride and carbon dioxide. Pioneering work in the UW phytoremediation labs has demonstrated biochemical pathways for plant transformations of trichloroethylene and carbon tetrachloride. We are also developing transgenic plants for the enhanced breakdown of chlorinated hydrocarbons. Another class of soluble compounds are some of the chemicals found in munitions, especially triazines such as RDX. We are also engineering plants to degrade these dangerous pollutants.



Insoluble compounds (hydrophobic)

Less soluble organic pollutants include polyaromatic hydrocarbons (**PAHs**) and polychlorinated biphenyls, as well as the munitions compound, TNT. Plants have a limited capability to take up these pollutants, but bacteria associated with their roots play a role in the degradation of many of these chemicals. The data sources used for this report contain information on only one application of phytoremediation to treat arsenic at full scale and two at pilot scale. Experimental research into identifying appropriate plant species for phytoremediation is ongoing. It is generally applicable only to shallow soil or relatively shallow groundwater that can be reached by plant roots. In addition, the phytoremediating plants may accumulate high levels of arsenic during the phytoremediation process, and may require additional treatment prior to disposal.

Technology Description: Phytoremediation is designed to use plants to degrade, extract, contain, or immobilize contaminants in soil, sediment, or groundwater (Ref. 15.6). Typically, trees with deep roots are applied to groundwater and other plants are used for shallow soil contamination.

Media Treated:

- . Soil
- . Groundwater

Types of Plants Used in Phytoremediation to Treat Arsenic:

- . Poplar
- . Cottonwood
- . Sunflower
- . Indian mustard
- . Corn

Technology Description and Principles

Phytoremediation is an emerging technology generally applicable only to shallow contamination that can be reached by plant roots.

Phytoremediation applies to all biological, chemical, and physical processes that are influenced by plants and the rhizosphere, and that aid in cleanup of the contaminated substances.

Phytoremediation may be applied in situ or ex situ, to soils, sludges, sediments, other solids, or groundwater (Ref. 15.1, 15.4, 15.5, 15.7). The mechanisms of phytoremediation include phytoextraction (also known as phytoaccumulation, the uptake of contaminants by plant roots and the translocation/accumulation of contaminants into plant shoots and leaves), enhanced rhizosphere biodegradation (takes place in soil or groundwater immediately surrounding plant roots), phytodegradation (metabolism of contaminants within plant tissues), and phytostabilization (production of chemical compounds by plants to immobilize contaminants at the interface of roots and soil).

The data sources used for this course identified phytoremediation applications for arsenic using phytoextraction and phytostabilization. The selection of the phytoremediating species depends upon the species ability to treat the contaminants and the depth of contamination. Plants with shallow roots (for example, grasses, corn) are appropriate only for contamination near the surface, typically in shallow soil. Plants with deeper roots, (for example, trees) may be capable of remediating deeper contaminants in soil or groundwater plumes.

Examples of vegetation used in phytoremediation include sunflower, Indian mustard, corn, and grasses (such as ryegrass and prairie grasses) (Ref. 15.1). Some plant species, known as hyperaccumulators, absorb and concentrate contaminants within the plant at levels greater than the concentration in the surrounding soil or groundwater. The ratio of contaminant concentration in the plant to that in the surrounding soil or groundwater is known as the bioconcentration factor.

A hyperaccumulating fern (*Pteris vittata*) has been used in the remediation of arsenic-contaminated soil, waste, and water. The fern can tolerate as much as 1,500 parts per million (ppm) of arsenic in soil, and can have a bioconcentration factor up to 265. The arsenic concentration in the plant can be as high as 2 percent (dry weight) (Ref. 15.3, 15.6).

Factors Affecting Phytoremediation Performance

Contaminant depth - The treatment depth is limited to the depth of the plant root system (Ref. 15.5).

Contaminant concentration - Sites with low to medium level contamination within the root zone are the best candidates for phytoremediation processes (Ref. 15.4, 15.5).

High contaminant concentrations may be toxic to the remediating flora.

Climatic or seasonal conditions – Climatic conditions may interfere or inhibit plant growth, slow remediation efforts, or increase the length of the treatment period (Ref. 15.4).

Contaminant form - In phytoaccumulation processes, contaminants are removed from the aqueous or dissolved phase.

Phytoaccumulation is generally not effective on contaminants that are insoluble or strongly bound to soil particles.

Agricultural factors - Factors that affect plant growth and health, such as the presence of weeds and pests, and the availability of sufficient water and nutrients will affect phytoremediation processes.

Media and Contaminants Treated

Phytoremediation has been applied to contaminants from soil, surface water, groundwater, leachate, and municipal and industrial wastewater (Ref. 15.4). In addition to arsenic, examples of pollutants it can potentially address include petroleum hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX), polycyclic aromatic hydrocarbons (PAHs), pentachlorophenol, polychlorinated biphenyls (PCBs), chlorinated aliphatics (trichloroethylene, tetrachloroethylene, and 1,1,2,2-tetrachloroethane), ammunition wastes (2,4,6- trinitrotoluene or TNT, and RDX), metals (lead, cadmium, zinc, arsenic, chromium, selenium), pesticide wastes and runoff (atrazine, cyanazine, alachlor), radionuclides (cesium-137, strontium-90, and uranium),

and nutrient wastes (ammonia, phosphate, and nitrate) (Ref. 15.7).

Treating Soil, Waste, and Water Containing Arsenic

The data sources used for this report contain information on phytoremediation of arsenic contaminated soil at full scale at one Superfund site (Ref. 15.7). Two pilot-scale applications and four bench-scale tests were also identified (Ref. 15.2, 15.3, 15.7-11).

Scale of Identified Phytoremediation Projects for Arsenic Treatment

Data on the effect of phytoremediation on the leachability of arsenic from soil were not identified. No projects with arsenic concentrations in the treated soil, waste, and water both prior to and after treatment were identified. Bioconcentration factors were available for one pilot- and two bench-scale studies, and ranged from 8 to 320.

Applicability, Advantages, and Potential Limitations

Phytoremediation is conducted in situ and therefore does not require soil excavation. In addition, revegetation for the purpose of phytoremediation also can enhance restoration of an ecosystem (Ref. 15.5).

This technology is best applied at sites with shallow contamination. If phytostabilization is used, the vegetation and soil may require long-term maintenance to prevent re-release of the contaminants. Plant uptake and translocation of metals to the aboveground portions of the plant may introduce them into the food chain if the plants are consumed (Ref. 15.5).

Products could bioaccumulate in animals that ingest the plants (Ref. 15.4). In addition, the toxicity and bioavailability of contaminants absorbed by plants and phytodegradation

products is not always known. Concentrations of contaminants in hyperaccumulating plants are limited to a maximum of about 3% of the plant weight on a dry weight basis. Based on this limitation, for fast-growing plants, the maximum annual contaminant removal is about 400 kg/hectare/year.

However, many hyperaccumulating species do not achieve contaminant concentrations of 3%, and are slow growing. (Ref. 15.12) The case study at the end of this section further discusses an application of phytoremediation to the treatment to arsenic-contaminated soil.

Factors Affecting Phytoremediation Costs

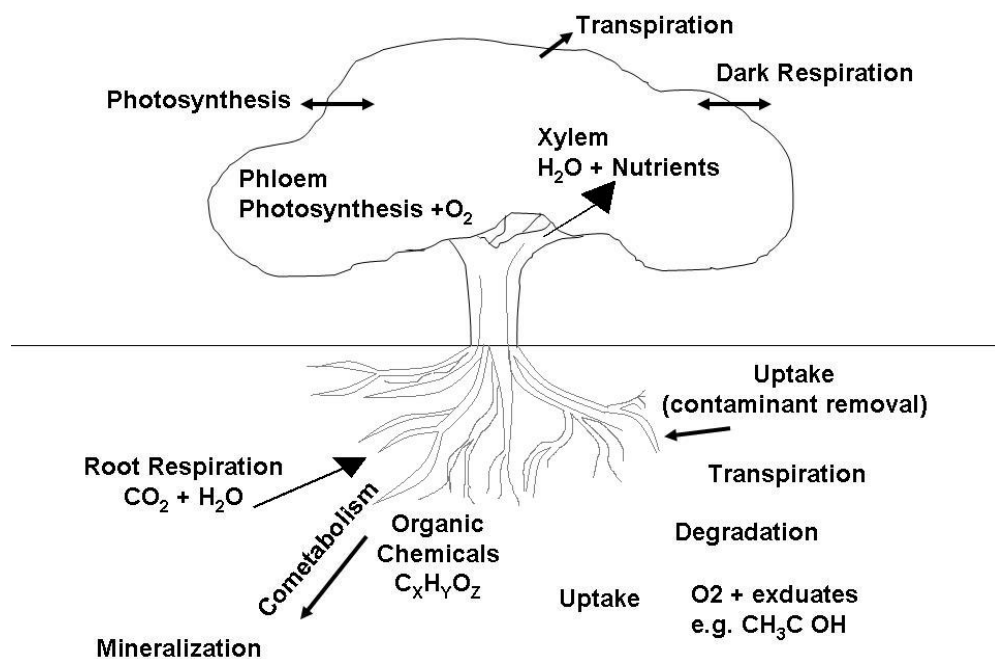
Number of crops grown - A greater number of crops may decrease the time taken for contaminants to be remediated to specified goals, thereby decreasing costs (Ref. 15.2).

However, the number of crops grown will be limited by the length of the growing season, the time needed for crops to reach maturity, the potential for multiple crops to deplete the soil of nutrients, climatic conditions, and other factors.

Summary of Cost Data

Cost data specific to phytoremediation of arsenic were not identified. The estimated 30-year costs (1998 dollars) for remediating a 12-acre lead site were \$200,000 for phytoextraction (Ref. 15.15). Costs were estimated to be \$60,000 to \$100,000 using phytoextraction for remediation of one acre of 20-inch-thick sandy loam (Ref. 15.14).

The cost of removing radionuclides from water with sun-flowers has been estimated to be \$2 to \$6 per thousand gallons of water (Ref. 15.16). Phytostabilization system costs have been estimated at \$200 to \$10,000 per hectare, equivalent to \$0.02 to \$1.00 per cubic meter of soil, assuming a 1-meter root depth (Ref. 15.17).



Model of Phytoremediation

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Biological Treatment for Arsenic

Biological treatment designed to remove arsenic from soil, waste, and water is an emerging remediation technology. The information sources used for this report identified a limited number of projects treating arsenic biologically. Arsenic was reduced to below 0.050 mg/L in one pilot-scale application.

This technology promotes precipitation/coprecipitation of arsenic in water or leaching of arsenic in soil and waste. The leachate from bioleaching requires additional treatment for arsenic prior to disposal.

Technology Description: Biological treatment of arsenic is based on the theory that microorganisms that act directly on arsenic species or create ambient conditions that cause arsenic to precipitate/coprecipitate from water and leach from soil and waste.

Media Treated:

- Soil
- Waste
- Water

Microbes Used:

- Sulfate-reducing bacteria
- Arsenic-reducing bacteria

Technology Description and Principles

Although biological treatments have usually been applied to the degradation of organic contaminants, some innovative techniques have applied biological remediation to the treatment of arsenic. This technology involves biological activity that promotes precipitation/coprecipitation of arsenic from water and leaching of arsenic in soil and waste.

Biological precipitation/coprecipitation processes for water create ambient conditions intended to cause arsenic to precipitate/coprecipitate or act directly on arsenic species to transform them into species that are more amenable to precipitation/coprecipitation. The microbes may be suspended in the water or attached to a submerged solid substrate. Iron or hydrogen sulfide may also be added (Ref. 16.2, 16.3, 16.4, 16.4).

One water treatment process depends upon biological activity to produce and deposit iron oxides within a filter media, which provides a large surface area over which the arsenic can contact the iron oxides. The aqueous solution is passed through the filter, where arsenic is removed from solution through coprecipitation or adsorption to the iron oxides. An arsenic sludge is continuously produced (Ref. 16.3).

Another process uses anaerobic sulfate-reducing bacteria and other direct arsenic-reducing bacteria to precipitate arsenic from solution as insoluble arsenic sulfide complexes (Ref. 16.2). The water containing arsenic is typically pumped through a packed-bed column reactor, where precipitates accumulate until the column becomes saturated (Ref. 16.5). The arsenic is then stripped and the column is biologically regenerated (Ref. 16.2).

Hydrogen sulfide has also been used in suspended reactors to biologically precipitate arsenic out of solution (Ref. 16.2, 16.4).

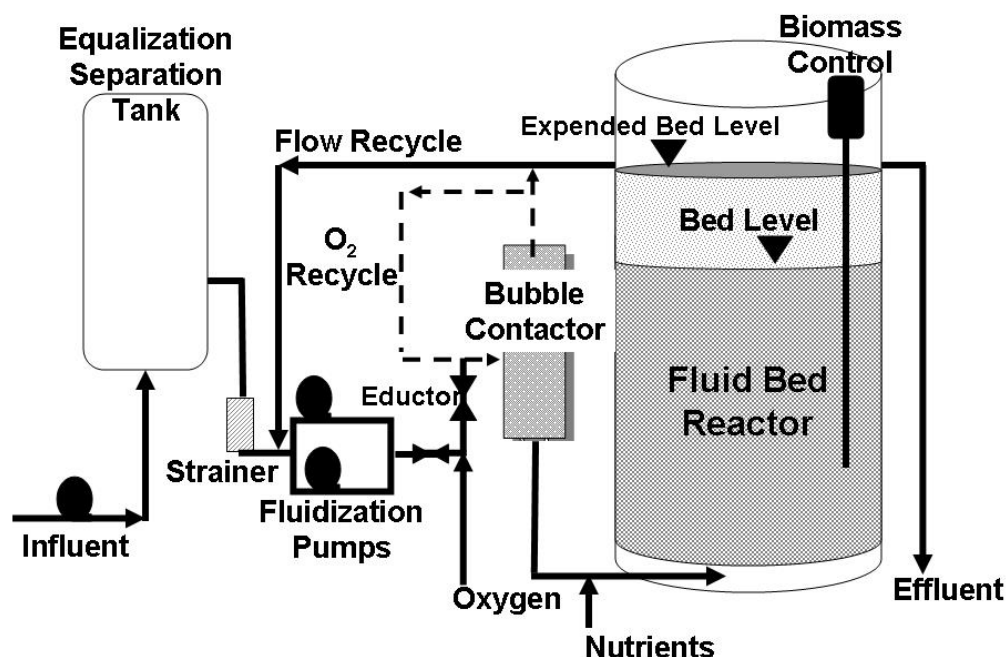
These reactors require conventional solid/liquid separation techniques for removing precipitates.

Removal of arsenic from soil biologically via “**accelerated bioleaching**” has also been tested on a bench scale. The microbes in this system produce nitric, sulfuric, and organic acids which are intended to mobilize and remove arsenic from ores and sediments (Ref. 16.4). This biological activity also produces surfactants, which can enhance metal leaching (Ref.16.4).

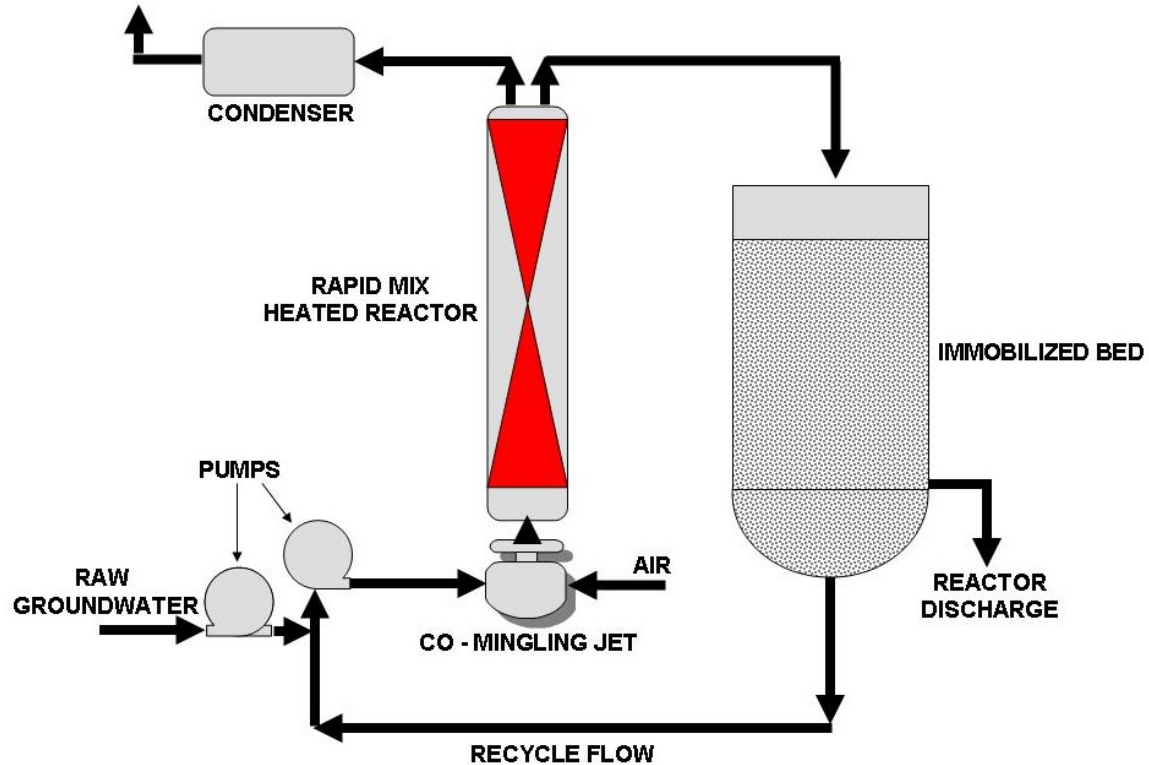
Types of Fixed Bioreactors

(these diagrams copied from: John T. Cookson, Jr., 1995. Bioremediation Engineering: Design and Application. McGraw-Hill, Inc, New York, New York.)

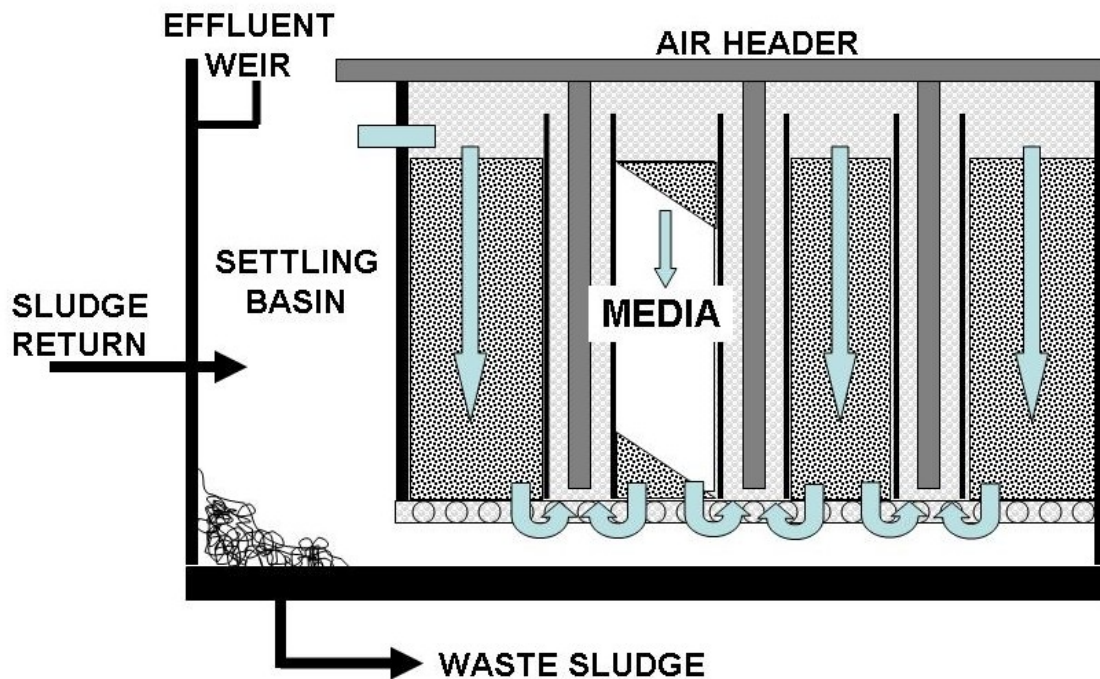
Fluidized Bed Bioreactor System



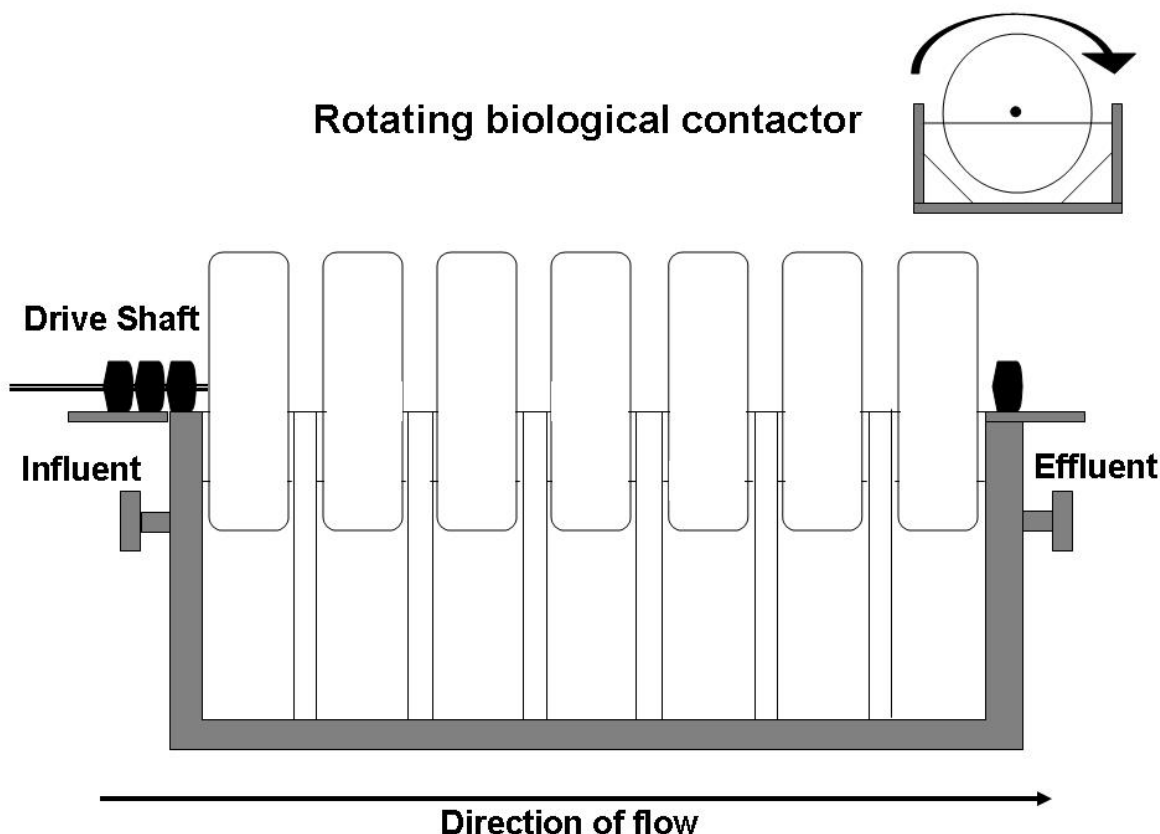
Packed Bed Reactor



Air Sparged Fixed-Bed Reactor



Rotating Media Reactor



Media and Contaminants Treated

Biological treatment typically uses microorganisms to degrade organic contaminants in soil, sludge, solids groundwater, and wastewaters.

Factors Affecting Biological Treatment Performance

- **pH** - pH levels can inhibit microbial growth. For example, sulfate-reducing bacteria perform optimally in a pH range of 6.5 to 8.0 (Ref. 16.5).
- **Contaminant concentration** - High arsenic concentrations may be toxic to microorganisms used in biological treatment (Ref. 16.1).
- **Available nutrients** - An adequate nutrient supply should be available to the microbes to enhance and stimulate growth. If the initial solution is nutrient deficient, nutrient addition may be necessary.
- **Temperature** - Lower temperatures decrease biodegradation rates. Heating may be required to maintain biological activity (Ref. 16.1).
- **Iron concentration** - For biologically enhanced iron precipitation, iron must be present in the water to be treated. The optimal iron level depends primarily on the arsenic concentration. (Ref. 16.3).

Factors Affecting Biological Treatment Costs

- **Pretreatment requirements** – Pretreatment may be required to encourage the growth of key microorganisms. Pretreatment can include pH adjustment and removal of contaminants that may inhibit microbial growth.

- **Nutrient addition** - If nutrient addition is required, costs may increase.

Treating Soil, Waste, and Water Containing Arsenic

The data sources used for this report contain information on biological treatment of arsenic at full scale at one facility, at pilot scale at three facilities, and at bench scale for one project. In addition, a biological treatment system using hydrogen sulfide has been used in a bio-slurry reactor to treat arsenic at bench and pilot scales (Ref. 16.4).

Applicability, Advantages, and Potential Limitations

A variety of arsenic-contaminated soil, waste, and water can be treated using biological processes. Biological treatment of arsenic may produce less sludge than conventional ferric arsenic precipitation (Ref. 16.2). A high concentration of arsenic could inhibit biological activity (Ref. 16.1, 16.2).

Case Study: Sodium Arsenite Spiked

Groundwater, Forest Row, Sussex, United Kingdom

Groundwater with naturally-occurring iron between 8 and 12 mg/L was extracted in Forest Row, Sussex, England and spiked with sodium arsenite.



The arsenic concentration before treatment ranged from 0.075 to 0.400 mg/L in the untreated water. The spiked groundwater was passed through a pilot biological filtration unit, 3 m high with a 15 cm diameter and filled to 1 m with silica sand. The arsenic concentration was reduced to <0.04 mg/L (Ref. 16.3)

Summary of Cost Data

The reported costs for biological treatment of arsenic contaminated soil, waste, and water range from less than \$0.50 to \$2.00 per 1,000 gallons (Ref. 16.2, 16.4, cost year not provided).

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Waste includes nonhazardous and hazardous solid waste generated by industry. Water includes groundwater, drinking water, non-hazardous and hazardous industrial wastewater, surface water, mine drainage, and leachate.

EPA Arsenic Waste Disposal

What Do I Need to Consider When Deciding on a Waste Disposal Option?

All arsenic treatment technologies, other than zero-treatment options such as alternate source use and blending, produce waste in the form of liquid residuals (e.g., brine, concentrates, filter rinse, and backwash), solid residuals (e.g., spent media, membranes, and dewatered sludge), or both. These residuals contain concentrated arsenic and other contaminants that must be disposed of properly.

Certain raw water characteristics can affect a system's waste disposal options and should be considered when selecting an arsenic treatment technology.

Raw water characteristics that may affect disposal alternatives include:

- ✓ Excessively high or low pH.
- ✓ High concentrations of competing ions (including fluoride, sodium, sulfate, and chloride).
- ✓ High total suspended solids (TSS).
- ✓ High total dissolved solids (TDS).
- ✓ High concentrations of heavy metals (including arsenic, lead, chromium, and aluminum).
- ✓ High concentrations of radionuclides.

The type of waste generated depends on the arsenic treatment technology selected. The following table shows the liquid and solid waste residuals that will be produced by likely small system treatment technologies.

You should work with your State to determine the best waste disposal option for your system based on your treatment processes, the type of

- ✓ waste generated, and the contaminant levels in the waste streams.

Selecting a Technology to Treat Arsenic

When choosing a technology, remember:

1. It is usually easier and cheaper to modify an existing treatment system than to install new treatment.
2. If you choose carefully, you may be able to install one technology to achieve compliance with the Arsenic Rule and other new rules. For more information on EPA's current and proposed regulations see www.epa.gov/safewater/regs.html or call the Safe Drinking Water Hotline at 1-800-426-4791.
3. You may need additional training to learn how to operate and maintain a new treatment process.
4. Most treatment technologies are more effective when the source water is pre-treated.
5. You should consider all options for waste disposal when you are choosing a treatment technology.
6. You should always pilot test a treatment method before installing it. Technologies are highly dependent on system specific considerations.
7. Your State may be able to help you choose an appropriate treatment technology.

For more information about treatment technologies and how they might work for you, ask your State or refer to:

- The *Arsenic Treatment Technology Design Manual for Small Systems* (EPA 816-R-02-011), available from EPA by calling the Safe Drinking Water Hotline at 1-800-426-4791.
- www.epa.gov/ogwdw000/ars/treat.html

Demonstration

EPA is conducting a demonstration program on the treatment of arsenic in drinking water. The Agency intends to identify and evaluate commercially available technologies, engineering options, or other approaches that cost-effectively help small systems (10,000 or fewer customers) meet the revised arsenic MCL. For more information on this program, see www.epa.gov/ORD/NRMRL/arsenic/.

Laboratory Testing

Certain analytical methods previously used by laboratories to measure arsenic concentrations are not sensitive enough to determine if your system is in compliance with the revised arsenic MCL of 0.010 mg/L. The methods that are no longer appropriate for compliance sampling are EPA method 200.7 and SM 3120B. The currently acceptable methods for compliance sampling are:

- ✓ EPA 200.8
- ✓ EPA 200.9
- ✓ SM 3113B
- ✓ SM 3114B
- ✓ ASTM D-2972-93B
- ✓ ASTM D-2972-93C

Contact your State if you are unsure about the method your lab normally uses.

What Does Compliance Monitoring Involve?

Monitoring Instructions

Routine Monitoring

If your monitoring results are at or below the revised MCL, you still must perform routine monitoring for arsenic at each sampling point (40 CFR 141.23(c)(1)):

- ✓ Once every 3 years during each nine year compliance cycle for ground water systems.
- ✓ Annually for surface water and GWUDI systems.

Waivers

Your State may issue you a waiver to reduce your monitoring frequency if your system historically has had arsenic levels below the revised MCL. Waivers allow you to take one sample during each 9-year compliance cycle. To be eligible for a waiver, you must have sampling results from three previous compliance periods (see Routine Monitoring, above) that (40 CFR 141.23(c)):

- ✓ Were collected at each sampling point.
- ✓ All were analyzed using analytical methods approved by the Arsenic Rule.
- ✓ All have arsenic levels below 0.010 mg/L.

For example, the system described in the Arsenic Planning Worksheet monitored during the previous three compliance periods (i.e., in 1998, 2001, and 2004). The system also collected samples from each sampling point and analyzed them using approved analytical methods. Since all of the results were below 0.010 mg/L, this system may be eligible for a waiver. Note that, in 1992, the system used analytical method SM 3120B. This method is not approved for compliance with the revised MCL, so the data from 1992 could not be used to satisfy the waiver eligibility requirements. In addition, the system did not sample from each sampling point in 1995. Therefore, these data do not meet the waiver requirements.

Increased Monitoring

Even if you are in compliance with the MCL, your State may require you to monitor more frequently (40 CFR 141.23(g)). Please contact your State for more information.

Compliance Determination

If the arsenic concentration in any of your samples exceeds 0.010 mg/L, your State may direct you to take a confirmation sample within 2 weeks (40 CFR 141.23(f)(1)). If the average of the initial sample and the confirmation sample is over 0.010 mg/L, you must begin quarterly monitoring at that sampling point (40 CFR 141.23(f)(3)&(c)(7)).

Calculate compliance with the MCL based on the running annual average, which is the sum of your results from the previous four quarters divided by the number of samples taken (40 CFR 141.23(i)(2)). You will be in violation when the running annual average exceeds 0.010 mg/L.

- You must divide the sum of the sample results from the previous four quarters by the number of samples taken. For example, if you failed to sample in one quarter, add the results from the other three quarters and divide by 3.
- During your first year of quarterly sampling, you will not yet have four quarters of results. In this case, you can assume the best case scenario when calculating the running annual average. Results for all future quarters (within the first year) can be entered as 0.0 mg/L.

Sampling and Reporting Notes

The four quarters are:

Q1: January - March

Q2: April - June

Q3: July - September

Q4: October - December

When you calculate your running annual average, use 0.0 mg/L for all samples with arsenic levels below what the analytical method can detect. If your State allows you to take more than the required number of samples, all of your samples will be averaged to determine compliance.

Monitoring and Reporting Violations

You have committed a monitoring and reporting (M&R) violation if:

- You fail to take a sample;
- You do not sample from each sampling point; or,
- You do not report your results to the State on time.

Maximum Contaminant Level Violations

If the running annual average of arsenic at a sampling point is greater than 0.010 mg/L, your system is in violation of the MCL (40 CFR 141.23(i)(1)). If you monitor once a year or less and the result from the initial sample (or the average of the results from the initial and confirmation samples) is greater than 0.010 mg/L but not more than 0.040 mg/L, your system has not yet violated the MCL. Having a result greater than 0.010 mg/L will require you to collect quarterly samples. If your system has an MCL violation, you must continue quarterly sampling until your State determines that your system is reliably and consistently below the MCL.

Reporting and Notification Requirements

Keeping the State and your customers informed is part of your responsibility as a public water system. The State needs to know if your system poses any health risks so it can help you protect your customers. Informed customers are more likely to understand the need for a new treatment system, infrastructure changes, and rate increases.

If you have an *M&R violation*, you must (40 CFR 141.31(b) & 141.204):

- ✓ Report this violation to the State within 48 hours of when the violation occurs.
- ✓ Notify your customers within a year. You may be able to incorporate this information into your CCR instead of a separate notification.

If you have an *MCL violation*, you must (40 CFR 141.31(b) & 141.203):

- ✓ Report this violation to the State within 48 hours of receiving the lab results.
- ✓ Notify your customers within 30 days.

In both cases, you must send a copy of any public notice to the State. If you are ***in compliance***, you must report your results and running annual average, if any, to the State within 10 days after the end of the month in which the sample was taken, or within 10 days of the end of the sampling period, whichever is shorter (40 CFR 141.31(a)).

In your annual ***Consumer Confidence Report***, you must include a statement about arsenic if monitoring results exceed 0.005 mg/L (40 CFR 141.153(d)(6) and 141.154(b)&(f)). See page 12 of this guide for more information.

Monitoring Worksheets

Depending on your source water and your previous arsenic results, you may be required to take samples quarterly, annually, once every 3 years, or once every 9 years.

These monitoring worksheets will help you:

- Collect the correct number of samples for each sampling period.
- Report monitoring results to your State on time.
- Collect appropriate confirmation samples.
- Know when your system is in violation of the arsenic MCL.
- Report MCL violations to your State and your customers on time.

Several copies of each worksheet are provided. The first copy is followed by instructions on how to complete it. The second copy is an example. The third is a blank worksheet that you can photocopy and use. Please note that your State may have a monitoring form of its own that must be used to submit sample results. If that is the case, the worksheets provided here **do not** replace the State form.

Appendix A: Sources for More Information on Arsenic

- ✓ The final text of the Arsenic Rule: EPA-815-Z-01-001 or Federal Register Vol. 66, No 14., pp. 6976-7066. The document is also available on line at www.epa.gov/safewater/ars/arsenic_finalrule.html.
- ✓ The Arsenic Implementation Guidance, EPA-816-D-01-002: www.epa.gov/safewater/ars/implement.html (available September 2002).
- ✓ EPA's Safe Drinking Water Hotline: 1-800-426-4791
- ✓ EPA's Safewater Web site (www.epa.gov/safewater/arsenic.html) has a number of documents including the text of the Arsenic Rule, the Arsenic Implementation Guidance, many fact sheets, and a quick reference guide to the Rule.
- ✓ American Water Works Association: www.awwa.org
- ✓ Association of State Drinking Water Administrators: www.asdwa.org
- ✓ National Ground Water Association: www.ngwa.org
- ✓ National Rural Water Association: www.nrwa.org
- ✓ Natural Resources Defense Council: www.nrdc.org/water/drinking/qarsenic.asp
- ✓ U.S. Congressional Research Service—*Report for Congress: Arsenic in Drinking Water-Recent Regulatory Developments and Issues:*
<http://cnie.org/NLE/CRSreports/water/h2o-40.cfm>

The World Health Organization: www.who.int/pes/ehc/summaries/ehc_224.html

Summaries of EPA Arsenic Publications - Arsenic

Regulations on the Disposal of Arsenic Residuals from Drinking Water Treatment Plants

EPA 600-R-00-025

As with other production processes, water treatment systems produce a product and a residual of that product. With the passage of the various federal statutes, restrictions have been placed on the discharge of residuals to water bodies and onto land. This report summarizes federal regulations and selected state regulations that govern the management of residuals produced by small drinking water treatment systems removing arsenic from drinking water.

Arsenic is a naturally occurring contaminant in ground water and many small water treatment facilities use ground water as their primary source of water. Under the Safe Drinking Water Act (SDWA), a maximum contaminant level (MCL) of 0.05 mg/L has been established for arsenic in drinking water. Under the 1996 SDWA Amendments, the EPA is required to develop a revised arsenic regulation by January 2001. Concerns have been raised as to the technical feasibility and regulatory implication of a more stringent arsenic MCL on the disposal of the residuals from arsenic removal processes. This document reports on five water treatment processes known to be effective for arsenic removal from small ground water systems. The five processes are anion exchange, activated alumina adsorption, iron/manganese removal, media adsorption, and membrane processes. For each technology, a brief description is provided of the treatment process along with a discussion of the residual production characteristics.

An overview is provided of the federal regulations that apply to the management of residuals, with a focus on arsenic removal residuals. The purpose of this overview is to provide guidance to water suppliers on the federal regulatory requirements of residuals management to better evaluate compliance of existing practices and to plan for needed changes in treatment plant operations. Specific disposal methods are summarized by the form of the residuals including liquid residuals (direct discharges, indirect discharges, underground injection, and land disposal) and solid/sludge residuals (solid waste landfill, hazardous waste landfill, lagoons, reuse of hazardous waste, reuse of solid waste, and off-site disposal) and the method in which the residuals are managed. Federal regulations summarized include the Clean Water Act (NPDES, Pretreatment), SDWA (Underground Injection Control and lagoons), and Resource Conservation and Recovery Act (Subtitles C/D). In addition to the federal regulations that impact the management of arsenic drinking water treatment residuals, regulations imposed by seven states were also reviewed.

The seven states (Arizona, California, Maine, Nebraska, New Mexico, Nevada, and Pennsylvania) were chosen based on arsenic occurrence and regional representation. The review of the state regulations also focused on characterizing the requirements that apply to different management options available for liquid and solid residuals generated by treatment systems that remove arsenic from drinking water. It was found that many components of the state regulatory programs were generally consistent with the federal minimum requirements.

Arsenic Removal from Drinking Water by Coagulation/filtration and Lime Softening Plants

EPA 600-R-00-063

This report documents treatment plant information as well as results of sampling and analysis at two coagulation/filtration plants (referred to in this document as Plants A and B) and one lime softening plant (referred to as Plant C). The objective of sampling and analysis was to evaluate the effectiveness of the water treatment plants to consistently remove arsenic (As) from source water. Additionally, data were collected in this study to evaluate the characteristics of the residuals produced by the treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation. The first phase, source water sampling, was conducted to evaluate source water characteristics at each plant. The second phase, preliminary sampling, consisted of a four-week sampling period to refine procedures prior to implementing the long-term evaluation phase. The third phase, long-term evaluation, consisted of weekly sample collection and analysis for approximately 1 year. Sludge samples also were collected at each facility during a single sampling event from settling lagoons/ponds during a two-month period.

Samples of recycle supernatant water (Plant A) and supernatant discharge water (Plants B and C) were collected monthly beginning in November 1998 and continuing until June 1999. Long-term evaluation of Plants A and B demonstrated that conventional coagulation/filtration can consistently achieve low levels of arsenic in the treated water (i.e., less than 5 µg/L). The total arsenic concentrations at Plant A were reduced by an average of 52%, which represents a decrease of average arsenic concentrations from 7.5 µg/L in the source water to 3.5 µg/L in the finished water. Average total arsenic removal efficiency at Plant B was 79%, with an average source water concentration of 19.1 µg/L and an average finished water concentration of 4.0 µg/L. Adsorption and coprecipitation of As(V) with iron and aluminum flocs are believed to have been the primary arsenic removal mechanisms at these plants.

The lime softening facility, Plant C, was not able to consistently reduce arsenic to low levels in treated water. The average total arsenic concentration in Plant C source water was 32.0 µg/L, and the lime softening plant reduced the average total arsenic concentration to 16.6 µg/L in the finished water, which equals a 45% removal efficiency. As(III) was the primary species of soluble arsenic in the raw water and was almost completely oxidized to As(V) as a result of two chlorination steps that occurred prior to softening and prior to filtration. The primary mechanism of arsenic removal was likely adsorption and coprecipitation of As(V) with iron that was present in the source water. Plant C operated at a pH of 9.6, a level at which arsenic removal by coprecipitation with calcium carbonate is reported to be less than 10% (Sorg and Logsdon, 1978; McNeill and Edwards, 1997b).

None of the sludge samples collected at Plants A, B, and C qualified as a hazardous waste based on Toxicity Characteristic Leaching Procedure (TCLP) testing for metals. Therefore, nonhazardous waste landfills should be able to accept the sludge generated by these treatment processes.

Arsenic Removal from Drinking Water by Iron Removal Plants

EPA 600-R-00-086

This report documents treatment plant information as well as results of sampling and analysis at two iron removal plants (referred to as Plants A and B). The objective of sampling and analysis was to evaluate the effectiveness of the water treatment plants to consistently remove arsenic (As) from source water. Additionally, data were collected in this study to evaluate the chemical characteristics of residuals produced by the treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation. The first phase, source water sampling, was conducted to evaluate source water characteristics at each plant. The second phase, preliminary sampling, was initiated at Plant A in April 1998 and at Plant B in May 1998. This phase consisted of a four-week sampling period to refine procedures for subsequent events during the third phase. The third phase, long-term evaluation, consisted of weekly sample collection and analysis beginning in June 1998 and continuing through June 1999 at Plant A and through December 1998 at Plant B. Plant personnel conducted all sampling during the long-term evaluation phase and Battelle coordinated sampling logistics. Sludge samples also were collected at Plant A during a single sampling event from an outdoor settling pond in November 1998. Samples of supernatant discharge (Plant A) and recycle supernatant (Plant B) were collected monthly beginning in November 1998 and continuing until June 1999 at Plant A and until January 1999 at Plant B.

Results from the long-term evaluation phase were varied regarding the ability of the iron removal process to consistently achieve low-level arsenic concentrations (e.g., $<5 \mu\text{g/L}$ in the finished water). The total arsenic concentrations at Plant A were reduced by an average of 87%, which represents a decrease in average arsenic concentration from $20.3 \mu\text{g/L}$ to $3.0 \mu\text{g/L}$.

Adsorption and coprecipitation with iron hydroxide precipitates are believed to be the primary arsenic removal mechanisms. The total arsenic concentrations at Plant B were reduced by an average of 74%, which represents a decrease in average arsenic concentration from $48.5 \mu\text{g/L}$ to $11.9 \mu\text{g/L}$. At Plant B, it appeared that only the particulate arsenic in the source water was removed. This particulate arsenic was most likely associated with the oxidized iron particles present in the source water (i.e., arsenic sorbed onto iron particles).

The primary difference in arsenic removal efficiency at Plants A and B is believed to be the amount of iron in the source water. Source water at Plant A averaged $2,284 \mu\text{g/L}$ of iron, while Plant B averaged $1,137 \mu\text{g/L}$. Increasing the iron in the source water at Plant B using a coagulant, such as ferric chloride, would likely enable Plant B to consistently achieve lower levels of arsenic. None of the sludge samples collected at Plant A qualified as a hazardous waste based on the Toxicity Characteristic Leaching Procedure (TCLP) test for metals. Therefore, nonhazardous waste landfills should be able to accept the sludge generated by this treatment facility. Stricter hazardous waste classification regulations in some states, such as California, on total arsenic concentrations in solid waste also were met at Plant A. Sludge samples were not collected at Plant B; however, analytical results were provided from a 1994 sludge sampling event.

Arsenic Removal from Drinking Water by Ion Exchange and Activated Alumina Plants

EPA 600-R-00-088

This report documents treatment plant information as well as results of year-long sampling and analysis at two ion exchange (IX) plants (referred to as Plants A and B) and two activated alumina (AA) plants (referred to as Plants C and D), with capacities varying from 800 to 3,000 gallons per day (gpd). The objective of sampling and analysis was to evaluate the performance of the full-scale water treatment plants to consistently remove arsenic from source water. Additionally, data were collected to evaluate the chemical characteristics of residuals produced by these treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation. Source water sampling was conducted to evaluate source water characteristics at each plant. Preliminary sampling was initiated in August 1998 and consisted of four sampling events conducted at each facility on either a weekly or biweekly basis to refine procedures for subsequent events during the third phase. Long-term evaluation consisted of weekly or biweekly sampling at each facility from September 1998 to September 1999.

Samples from resin regeneration were collected at Plant A from March to June 1999. Spent AA samples were collected at Plants C and D during the media change-out events in December 1998 and May 1999, respectively. Results from the long-term evaluation demonstrated that both the IX and AA systems are capable of achieving arsenic levels of less than 5 µg/L in the treated water, provided that the IX resin was regenerated or the AA medium was changed out before arsenic breakthrough occurred. The two IX systems had inlet arsenic concentrations between 45 and 65 µg/L [primarily As(V)].

When Plant A was operated beyond 3,000 to 3,200 bed volumes (BV) of water, arsenic chromatographic peaking occurred. Arsenic breakthrough was not observed at Plant B where an average 97% of removal efficiency was achieved, leaving only 0.8 to 4.5 µg/L arsenic in the finished water. Both AA systems consisted of two parallel treatment trains with a roughing AA column followed by a polishing column in each train.

The systems operated on a media throwaway basis. The average arsenic removal efficiencies achieved at Plants C and D were 87% and 98%, respectively. The raw water at Plant C (34 to 76 µg/L total arsenic) contained approximately 0.3 to 28.8 µg/L As(III), which was nearly completely removed, even though no oxidation treatment was provided. The water at Plant D contained slightly higher total arsenic concentrations (53.3 to 87 µg/L) but no As(III), which was consistently removed to less than 5 µg/L in the finished water.

The AA media in the roughing tanks were exhausted and disposed of about every 1 to 1.5 years after treating approximately 9,600 BV at Plant C and 5,260 BV at Plant D. The regeneration process at Plant A recovered from 67 to 86% of arsenic from the spent brine. The spent AA at Plants C and D passed the Toxicity Characteristic Leaching Procedure (TCLP) test for metals including arsenic, and therefore was disposed of as nonhazardous waste.

Laboratory Study on the Oxidation of Arsenic III to Arsenic V

EPA 600-R-01-021

A one-year laboratory study was performed to determine the ability of seven oxidants to oxidize As(III) to As(V). These included chlorine, permanganate, ozone, chlorine dioxide, monochloramine, a solid-phase oxidizing media, and 254 nm ultraviolet light. Chlorine and permanganate rapidly oxidized As(III) to As(V) in the pH range of 6.3 to 8.3. Dissolved manganese, dissolved iron, sulfide and TOC slowed the rate of oxidation slightly, but essentially complete oxidation was obtained in less than one minute with chlorine and permanganate under all conditions studied.

In the absence of interfering reductants, ozone rapidly oxidized As(III). Although, dissolved manganese and dissolved iron had no significant effect on As(III) oxidation, the presence of sulfide considerably slowed the oxidation reaction. The presence of TOC had a quenching effect on As(III) oxidation by ozone, producing incomplete oxidation at the higher TOC concentration studied. Only limited As(III) oxidation was obtained using chlorine dioxide, which was probably due to the presence of chlorine (as a by-product) in the chlorine dioxide stock solutions. The reason for the ineffectiveness of chlorine dioxide was not studied.

Preformed monochloramine was ineffective for As(III) oxidation, whereas limited oxidation was obtained when monochloramine was formed in-situ. This showed that the injected chlorine probably reacted with As(III) before being quenched by ammonia to form monochloramine. Filox, a manganese dioxide-based media, was effective for As(III) oxidation. When dissolved oxygen (DO) was not limiting, complete oxidation was observed under all conditions studied.

However, when DO was reduced, incomplete oxidation was obtained in the presence of interfering reductants. The adverse effect of interfering reductants was completely eliminated by either (a) supplying enough DO or (b) increasing the contact time. In addition to oxidizing As(III), the Filox media also removed some arsenic by adsorption, which diminished greatly as the media came into equilibrium with the As(III)-spiked synthetic water.

UV light alone (254 nm) was not very effective for As(III) oxidation. Significant oxidation was observed only at very low flow rates representing 0.6 - 2.5% of the rated capacities of the two UV sterilizer units tested. However, as reported in a patented process, complete oxidation by UV light was observed when the challenge water was spiked with 1.0 mg/L sulfite.

Treatment of Arsenic Residuals from Drinking Water Removal Processes

EPA 600-R-01-033

The drinking water MCL was recently lowered from 0.05 mg/L to 0.01 mg/L. One concern was that a reduction in the TCLP arsenic limit in response to the drinking water MCL could be problematic with regard to disposal of solid residuals generated at arsenic removal facilities. This project focused on developing a short-list of arsenic removal options for residuals produced by ion exchange (Ion Ex), reverse osmosis (RO), nanofiltration (NF), activated alumina (AA), and iron removal processes. Both precipitation and adsorption processes were evaluated to assess their arsenic removal effectiveness.

In precipitation tests, ferric chloride outperformed alum for removal of arsenic from residuals by sedimentation, generally resulting in arsenic removals of 88 to 99 percent. Arsenic removal from the high alkalinity ion exchange samples was poorer. The required iron-to-arsenic molar ratio for best removal of arsenic in these screening tests varied widely from 4:1 to 191:1, depending on residuals type, and best arsenic removal using ferric chloride typically occurred between pH 5.0 and 6.2. Polymer addition typically did not significantly improve arsenic removal using either coagulant. Supernatant total arsenic levels of 0.08 mg/L or lower were attained with ferric chloride precipitation for membrane concentrates and residuals from iron removal facilities compared to an in-stream arsenic limit of 0.05 mg/L in place in some states. Settling alone with no coagulant also effectively removed arsenic from iron removal facility residuals.

Even with ferric chloride dosages of 50 to 200 mg/L applied to ion exchange regenerants, supernatant arsenic levels after treatment were 1 to 18 mg/L. Required iron-to-arsenic molar ratios developed in precipitation work could be used by utilities as guidelines for establishing coagulant dose needs to meet in-stream standards, and to develop preliminary treatment costs. Adsorption tests demonstrated the potential for different types of media and resins to remove arsenic from liquid residuals, but did not assess ultimate capacity.

Overall, the iron-based granular ferric hydroxide media evaluated in testing outperformed the aluminum-based media and ion exchange resin for removal of arsenic. However, activated alumina and the iron-based media provided comparable arsenic removals of close to 100 percent with an empty bed contact time (EBCT) of 3-min for most of the membrane concentrates and the settled iron removal facility residuals. Removal of suspended solids was key to the success of adsorption for spent filter backwash water and clarifier flush residuals. Arsenic breakthrough occurred very rapidly for the ion exchange samples and for one RO concentrate, all of which had an alkalinity of more than 1,000 mg/L (as CaCO₃). This again suggests that alkalinity significantly interferes with adsorption of arsenic. Based on this work, use of adsorption media for treatment of arsenic-laden water plant residuals merits further exploration.

Of all of the residuals streams tested, Ion Ex regenerants were the most difficult to treat using precipitation or adsorption. Disposal of supernatant streams resulting from treatment of arsenic-laden residuals from ion exchange plants could pose a major challenge. TCLP arsenic levels in all residuals generated in this work and in full-scale solid media samples were far below the regulatory limit of 5 mg/L, and in fact were below 0.5 mg/L.

Oxidation of As(III) by Aeration and Storage

EPA 600-R-01-102

A study of the effects of aeration and storage on the oxidation of arsenic(III) was undertaken at three utilities in the U.S. to establish the engineering significance of aeration as a potential pre-treatment method for arsenic removal. Aeration has been referred to in the literature as a possible useful pre-treatment method to ensure that arsenic is in the arsenic(V) state before subsequent removal by any of several treatment processes. Since aeration is a common process for treating groundwater for iron oxidation, radon, volatile organics, carbon dioxide, and hydrogen sulfide, it is reasonable to investigate its effectiveness for arsenic(III) oxidation.

The results of this study clearly establish that aeration and aerobic storage do not oxidize arsenic(III). The major conclusion is that aeration is not effective for this purpose and should not be relied upon or expected to contribute to the oxidation of arsenic(III). One of the test sites in this study clearly showed that arsenic(III) is significantly removed by the oxidation and precipitation of iron, but this should not be attributed to an oxidation of arsenic(III) to arsenic(V) by dissolved oxygen. Past research has established that iron precipitation can be partially effective for the adsorptive removal of arsenic(III), and this is the likely explanation for the apparent drop in arsenic(III) at the site that had high iron.

The effect of iron precipitation on the removal of arsenic was also present in the long term storage of aerated water in this study. When all of the iron (initial iron at 2.7 mg/L) precipitated from the quiescent storage water, the remaining aqueous total arsenic was entirely dissolved and in the arsenic(V) state. The aqueous arsenic(III) was below detection and apparently completely removed or converted by the insoluble iron.

Even in this case it is doubtful if DO was responsible for any oxidation of arsenic(III), because the loss directly correlated to the loss of iron precipitate and no other instance of arsenic(III) oxidation occurred at the other sites. In summary, the data supported the fact that iron is extremely important in the removal of arsenic(III), but did not support the idea that arsenic(III) is oxidized by aeration. This is true at least for the conditions used in this study.

While the subtleties of the results are interesting, especially for the site with high iron, it is important to emphasize the original objective of this study, which was to establish if typical aeration and storage methods could oxidize arsenic(III).

Based upon the results of this study, it is concluded that aeration does not oxidize arsenic(III) and that subsequent storage for up to five days does not result in arsenic(III) oxidation. Dissolved oxygen should not be considered as a candidate for arsenic(III) oxidation; however, aeration will continue to be considered a very effective process for the oxidation of iron. In that way, aeration can be said to be effective in bringing about the removal of As via the oxidative precipitation of iron.

Design Manual: Removal of Arsenic from Drinking Water by Adsorptive Media

EPA 600-R-03-019

This design manual is an in-depth presentation of the steps required to design and operate a water treatment plant for removal of excess arsenic from drinking water using the adsorptive media process. This treatment process is very reliable, simple and cost-effective. Several adsorptive media products are available in the market-place that have successfully demonstrated their capability to remove arsenic from drinking water to levels well below the revised MCL, 0.010 mg/L.

Other new products continue to be developed. The adsorptive media products are preferential for the removal of arsenic over other competing ions. Therefore, unless a water system requires treatment capability for removal of other suspended or dissolved contaminants, the adsorptive media treatment method merits evaluation.

The adsorptive media process is implemented with operational options which vary with the product selected. For water systems that are primarily concerned with financial feasibility, capital and operating costs, each operational option along with each available adsorptive media product should be evaluated. This design manual provides the methods for competently performing each evaluation.

The arsenic removal capacity of some adsorptive media products, such as activated alumina, are very sensitive to the pH of the water passing thru treatment. Others, such as iron-based products, are not. Treatment processes incorporating pH adjustment capability require careful handling and storage of corrosive chemicals (acid and caustic).

Some adsorptive media products, such as activated alumina, are capable of being chemically regenerated for repetition of treatment cycles using the same corrosive chemicals as those used for pH adjustment in the treatment process. Regeneration is not recommended for other adsorptive media products.

Whether or not pH of water being treated is adjusted, the adsorptive media can be replaced in place of regeneration upon exhaustion of arsenic capacity. This design manual presents the information necessary to design and operate treatment systems for any combination of operational options and for any adsorptive media. It also discusses the capital and operating costs including the many variables which can raise or lower costs for identical treatment systems.

Design Manual: Removal of Arsenic from Drinking Water by Ion Exchange

EPA 600-R-03-080

This design manual is an in-depth presentation of the steps required to design and operate a water treatment plant for removing arsenic in the As(V) form from drinking water using the anion exchange process. Because As(III) occurs as an uncharged anion in ground water in the pH range of 6.5 to 8, the process will not remove As(III) unless it is first oxidized to As(V). The manual also discusses the capital and operating costs, including many of the variables that can raise or lower costs for identical treatment systems.

The anion exchange treatment process is very reliable, simple, and cost-effective. The treatment process removes arsenic using a strong base anion exchange resin in either the chloride or hydroxide form, with chloride the preferred form because salt can be used as the regenerant. The process preferentially removes sulfate over arsenic; and, therefore, as the sulfate increases in the raw water, the process becomes less efficient and more costly. Furthermore, because sulfate occurs in significantly higher concentrations than arsenic, treatment run lengths are dependent almost entirely on the sulfate concentration of the raw water. The ion exchange process is a proven efficient and cost-effective treatment method for removing As(V) from water supplies with low sulfate levels.

The configuration of an anion exchange system for As(V) removal can take several forms. The method presented in this design manual uses three vertical cylindrical pressure vessels operating in a downflow mode. Two of the three treatment vessels are piped in parallel to form the primary arsenic removal stage.

The third treatment vessel is piped in series in the lag position. In the primary stage, raw water flows through one of the two treatment vessels while the second vessel is held in the standby position. When the treatment capacity of the first vessel approaches exhaustion, it is removed from service and replaced by the second primary stage vessel.

While out of service, the first vessel is regenerated and placed in the standby position. The role of the third treatment vessel in the lag position is to ensure that any arsenic that breaks (peaking) through one of the lead vessels does not enter the distribution system. Although this design concept results in higher capital costs, it prevents high arsenic concentrations in the treated water, if operated properly.

Capital Costs of Arsenic Removal Technologies Demonstration Program Round 1

EPA 600-R-04-201

On January 18, 2001, the U.S. Environmental Protection Agency (EPA) finalized the maximum contaminant level (MCL) for arsenic at 0.01 mg/L. EPA subsequently revised the rule text to express the MCL as 0.010 mg/L (10 µg/L). The final rule requires all community and non-transient, non-community water systems to comply with the new standard by February 2006. In October 2001, the EPA announced an initiative for additional research and development of cost-effective technologies to help small community water systems (<10,000 customers) meet the new arsenic standard, and to provide technical assistance to operators of small systems in order to reduce compliance costs.

As part of this Arsenic Rule Implementation Research Program, EPA's Office of Research and Development (ORD) proposed a project to conduct a series of full-scale, long-term, on-site demonstrations of arsenic removal technologies, process modifications, and engineering approaches applicable to small systems in order to evaluate the efficiency and effectiveness of arsenic removal systems at meeting the new arsenic MCL. For the Round 1 demonstration study, the selected arsenic treatment technologies include nine adsorptive media systems, one ion exchange system, one coagulation/filtration system, and one process modification. The adsorptive media systems use four different adsorptive media, including three iron-based media, i.e., ADI's G2, Severn Trent and AdEdge's E33, and USFilter's GFH, and one iron-modified activated alumina media, i.e., Kinetico's AAFS50 (a product of Alcan). Since the inception of the project, 10 of 12 systems have been installed, with flowrates at all systems ranging from 37 to 640 gpm.

A key objective of the long-term demonstration project is to determine the cost-effectiveness of the technologies. This report provides a brief description of each of the 12 Round 1 demonstration sites and the respective technologies being evaluated. Capital costs were organized into three categories—equipment, engineering, and installation—and then summed to arrive at a total capital investment cost for each system. Operations and maintenance (O&M) costs associated with the treatment systems are not yet available; however, vendor-supplied estimates on media replacement costs also are provided in this report.

Excluding the cost for one system modification site, the total capital investment costs range from \$90,757 to \$305,000, and vary by flowrate, system design, material of construction, monitoring equipment, and specific site conditions. Based on a 3% interest rate and a 20-year return period, the unit costs of the total capital investment range from \$0.03 to \$0.79 per 1,000 gallons of water treated. In general, the unit cost decreases as the size of a treatment system increases.

The equipment costs for the treatment systems range from \$66,235 to \$218,000, representing 54 to 80% of the total capital investment cost. Engineering costs for the treatment systems range from \$4,907 to \$50,659, accounting for 5 to 22% of the total capital investment with an average of 12%. Installation costs for the treatment systems range from \$13,150 to \$77,574, which accounts for 12 to 34% of the total capital investment with an average of 22%. Finally, building cost information obtained from the host facilities also is provided in the report. Building costs range from \$3,700 to \$186,000, varying according to differences in location, size, design, material of construction, and choice of construction contractor.

Technology Selection and System Design, USEPA Arsenic Demonstration Program Round 1

EPA 600-R-05-001

On January 18, 2001, the U.S. Environmental Protection Agency (EPA) finalized the maximum contaminant level (MCL) for arsenic at 0.01 mg/L. EPA subsequently revised the rule text to express the MCL as 0.010 mg/L (10 µg/L). The final rule requires all community and non-transient, non-community water systems to comply with the new standard by February 2006. In October 2001, EPA announced an initiative for additional research and development of cost-effective technologies to help small community water systems (<10,000 customers) meet the new arsenic standard, and to provide technical assistance to operators of small systems in order to reduce compliance costs.

As part of this Arsenic Rule Implementation Research Program, EPA's Office of Research and Development (ORD) proposed a project to conduct a series of full-scale, long-term, on-site demonstrations of arsenic removal technologies, process modifications, and engineering approaches applicable to small systems in order to evaluate the efficiency and effectiveness of arsenic removal systems at meeting the new arsenic MCL.

For the Round 1 demonstration study, the selected arsenic treatment technologies include nine adsorptive media systems, one ion exchange system, one coagulation /filtration system, and one process modification. The adsorptive media systems use four different adsorptive media, including three iron-based media (i.e., ADI's G2, Severn Trent and AdEdge's E33, and USFilter's GFH), and one iron-modified activated alumina media (i.e., Kinetico's AAFS50, a product of Alcan). The flowrate of these systems ranges from 37 to 640 gallons per minute (gpm).

This report provides the source water quality characteristics at each of the 12 demonstration sites and the general rationale used to select the technologies for demonstration at each site. Information on the design and operation of each treatment system also is presented. The selection of the technologies for demonstration at each location was a cooperative decision made by the water system, state, and EPA. Many factors were considered in the selection process, including water quality, residual production and disposal, complexity of system operation, and costs.

The selection of the adsorptive media and pretreatment methods depended on a number of factors that affect the system performance, including arsenic concentration and speciation, pH, and the presence of competing anions, as well as media-specific characteristics such as costs, media life, and empty-bed contact time (EBCT) requirements.

Using DWSRF Funds to Comply with the New Arsenic Rule

EPA 816-F-02-004

The Drinking Water State Revolving Fund (DWSRF) program was established by the 1996 Safe Drinking Water Act (SDWA) Amendments and authorizes grants to states to capitalize revolving loan funds. The states provide low-interest loans to eligible systems for infrastructure improvements needed to ensure compliance with the SDWA and protect public health. The DWSRF program can play a significant role in helping systems, especially small systems, to meet the challenges of complying with new drinking water standards.

The Environmental Protection Agency (EPA) published revisions to the Arsenic Rule in 2001 which further reduce exposure to arsenic in drinking water by adopting a new arsenic maximum contaminant level (MCL) of 10 ppb. The new MCL will impose a financial burden on some water systems. The DWSRF can provide assistance to systems to help ease this burden, increase compliance, and protect public health.

Rural Development-Rural Utilities Service, Loan, and Grant Program: Fact Sheet

EPA 816-F-03-009

USDA/Rural Development/Rural Utilities Service (RUS) administers water and wastewater loan and grant programs to improve the quality of life and promote economic development in Rural America. These programs were previously administered by the Farmers Home Administration (FmHA)

Implementation Guidance for the Arsenic Rule - Drinking Water Regulations for Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring

EPA 816-K-02-018

The final Implementation Guidance for the Arsenic Rule is based on the final rule published in the Federal Register on January 22, 2001. It incorporates comments received on the previous draft implementation guidances, and from the training sessions on the arsenic rule held throughout the country. The guidance summarizes key sections of the Proposed Rule and provides a "how to approach" for EPA Regions and States to implement the regulation. It contains an explanation of the rule's requirements and guidance for preparing State primacy revision applications. The document incorporates comments received from Regions, States, technical assistance providers, water systems, and others.

Regulations on the Disposal of Arsenic Residuals from Drinking Water Treatment Plants

EPA 600-R-00-025

As with other production processes, water treatment systems produce a product and a residual of that product. With the passage of the various federal statutes, restrictions have been placed on the discharge of residuals to water bodies and onto land. This report summarizes federal regulations and selected state regulations that govern the management of residuals produced by small drinking water treatment systems removing arsenic from drinking water.

Arsenic is a naturally occurring contaminant in ground water and many small water treatment facilities use ground water as their primary source of water. Under the Safe Drinking Water Act (SDWA), a maximum contaminant level (MCL) of 0.05 mg/L has been established for arsenic in drinking water. Under the 1996 SDWA Amendments, the EPA is required to develop a revised arsenic regulation by January 2001. Concerns have been raised as to the technical feasibility and regulatory implication of a more stringent arsenic MCL on the disposal of the residuals from arsenic removal processes.

This document reports on five water treatment processes known to be effective for arsenic removal from small ground water systems. The five processes are anion exchange, activated alumina adsorption, iron/manganese removal, media adsorption, and membrane processes. For each technology, a brief description is provided of the treatment process along with a discussion of the residual production characteristics.

An overview is provided of the federal regulations that apply to the management of residuals, with a focus on arsenic removal residuals. The purpose of this overview is to provide guidance to water suppliers on the federal regulatory requirements of residuals management to better evaluate compliance of existing practices and to plan for needed changes in treatment plant operations. Specific disposal methods are summarized by the form of the residuals including liquid residuals (direct discharges, indirect discharges, underground injection, and land disposal) and solid/sludge residuals (solid waste landfill, hazardous waste landfill, lagoons, reuse of hazardous waste, reuse of solid waste, and off-site disposal) and the method in which the residuals are managed.

Complying With the Revised Drinking Water Standard for Arsenic: Small Entity Compliance Guide

EPA 816-R-02-008A

This guide is designed for owners and operators of community water systems (CWSs) and non-transient non-community water systems (NTNCWSs) serving 10,000 or fewer persons. CWSs include all systems (regardless of ownership) serving at least 25 year-round residents or 15 year-round service connections. NTNCWSs include all systems (regardless of ownership) that are not CWSs and that regularly serve at least 25 of the same people for more than 6 months a year. Systems that will typically find this guide useful include:

- Small towns
- Rural water districts
- Tribal systems
- Mobile home parks

Federal regulations summarized include the Clean Water Act (NPDES, Pretreatment), SDWA (Underground Injection Control and lagoons), and Resource Conservation and Recovery Act (Subtitles C/D). In addition to the federal regulations that impact the management of arsenic drinking water treatment residuals, regulations imposed by seven states were also reviewed.

The seven states (Arizona, California, Maine, Nebraska, New Mexico, Nevada, and Pennsylvania) were chosen based on arsenic occurrence and regional representation. The review of the state regulations also focused on characterizing the requirements that apply to different management options available for liquid and solid residuals generated by treatment systems that remove arsenic from drinking water. It was found that many components of the state regulatory programs were generally consistent with the federal minimum requirements. However, the state programs differed from federal program requirements and each other in several aspects including surface water quality standards applicable to control the amount of arsenic in direct discharges of liquid effluent, the local limits that specify how much arsenic may be discharged to a sanitary sewer system, the regulation of solid waste landfills, the protection of ground water resources, and the regulation of land application activities.

Arsenic Removal from Drinking Water by Coagulation/filtration and Lime Softening Plants

EPA 600-R-00-063

This report documents treatment plant information as well as results of sampling and analysis at two coagulation/filtration plants (referred to in this document as Plants A and B) and one lime softening plant (referred to as Plant C). The objective of sampling and analysis was to evaluate the effectiveness of the water treatment plants to consistently remove arsenic (As) from source water. Additionally, data were collected in this study to evaluate the characteristics of the residuals produced by the treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation. The first phase, source water sampling, was conducted to evaluate source water characteristics at each plant. The second phase, preliminary sampling, consisted of a four-week sampling period to refine procedures prior to implementing the long-term evaluation phase. The third phase, long-term evaluation, consisted of weekly sample collection and analysis for approximately 1 year. Sludge samples also were collected at each facility during a single sampling event from settling lagoons/ponds during a two-month period.

Samples of recycle supernatant water (Plant A) and supernatant discharge water (Plants B and C) were collected monthly beginning in November 1998 and continuing until June 1999. Long-term evaluation of Plants A and B demonstrated that conventional coagulation/filtration can consistently achieve low levels of arsenic in the treated water (i.e., less than 5 µg/L). The total arsenic concentrations at Plant A were reduced by an average of 52%, which represents a decrease of average arsenic concentrations from 7.5 µg/L in the source water to 3.5 µg/L in the finished water. Average total arsenic removal efficiency at Plant B was 79%, with an average source water concentration of 19.1 µg/L and an average finished water concentration of 4.0 µg/L. Adsorption and coprecipitation of As(V) with iron and aluminum flocs are believed to have been the primary arsenic removal mechanisms at these plants.

The lime softening facility, Plant C, was not able to consistently reduce arsenic to low levels in treated water. The average total arsenic concentration in Plant C source water was 32.0 µg/L, and the lime softening plant reduced the average total arsenic concentration to 16.6 µg/L in the finished water, which equals a 45% removal efficiency. As(III) was the primary species of soluble arsenic in the raw water and was almost completely oxidized to As(V) as a result of two chlorination steps that occurred prior to softening and prior to filtration. The primary mechanism of arsenic removal was likely adsorption and coprecipitation of As(V) with iron that was present in the source water. Plant C operated at a pH of 9.6, a level at which arsenic removal by coprecipitation with calcium carbonate is reported to be less than 10% (Sorg and Logsdon, 1978; McNeill and Edwards, 1997b).

None of the sludge samples collected at Plants A, B, and C qualified as a hazardous waste based on Toxicity Characteristic Leaching Procedure (TCLP) testing for metals. Therefore, nonhazardous waste landfills should be able to accept the sludge generated by these treatment processes.

Arsenic Removal from Drinking Water by Iron Removal Plants

EPA 600-R-00-086

This report documents treatment plant information as well as results of sampling and analysis at two iron removal plants (referred to as Plants A and B). The objective of sampling and analysis was to evaluate the effectiveness of the water treatment plants to consistently remove arsenic (As) from source water. Additionally, data were collected in this study to evaluate the chemical characteristics of residuals produced by the treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation. The first phase, source water sampling, was conducted to evaluate source water characteristics at each plant. The second phase, preliminary sampling, was initiated at Plant A in April 1998 and at Plant B in May 1998. This phase consisted of a four-week sampling period to refine procedures for subsequent events during the third phase. The third phase, long-term evaluation, consisted of weekly sample collection and analysis beginning in June 1998 and continuing through June 1999 at Plant A and through December 1998 at Plant B. Plant personnel conducted all sampling during the long-term evaluation phase and Battelle coordinated sampling logistics. Sludge samples also were collected at Plant A during a single sampling event from an outdoor settling pond in November 1998. Samples of supernatant discharge (Plant A) and recycle supernatant (Plant B) were collected monthly beginning in November 1998 and continuing until June 1999 at Plant A and until January 1999 at Plant B.

Results from the long-term evaluation phase were varied regarding the ability of the iron removal process to consistently achieve low-level arsenic concentrations (e.g., $<5 \mu\text{g/L}$ in the finished water). The total arsenic concentrations at Plant A were reduced by an average of 87%, which represents a decrease in average arsenic concentration from $20.3 \mu\text{g/L}$ to $3.0 \mu\text{g/L}$. Adsorption and coprecipitation with iron hydroxide precipitates are believed to be the primary arsenic removal mechanisms. The total arsenic concentrations at Plant B were reduced by an average of 74%, which represents a decrease in average arsenic concentration from $48.5 \mu\text{g/L}$ to $11.9 \mu\text{g/L}$. At Plant B, it appeared that only the particulate arsenic in the source water was removed. This particulate arsenic was most likely associated with the oxidized iron particles present in the source water (i.e., arsenic sorbed onto iron particles).

The primary difference in arsenic removal efficiency at Plants A and B is believed to be the amount of iron in the source water. Source water at Plant A averaged $2,284 \mu\text{g/L}$ of iron, while Plant B averaged $1,137 \mu\text{g/L}$. Increasing the iron in the source water at Plant B using a coagulant, such as ferric chloride, would likely enable Plant B to consistently achieve lower levels of arsenic. None of the sludge samples collected at Plant A qualified as a hazardous waste based on the Toxicity Characteristic Leaching Procedure (TCLP) test for metals. Therefore, nonhazardous waste landfills should be able to accept the sludge generated by this treatment facility. Stricter hazardous waste classification regulations in some states, such as California, on total arsenic concentrations in solid waste also were met at Plant A. Sludge samples were not collected at Plant B; however, analytical results were provided from a 1994 sludge sampling event.

Arsenic Removal from Drinking Water by Ion Exchange and Activated Alumina Plants

EPA 600-R-00-088

This report documents treatment plant information as well as results of year-long sampling and analysis at two ion exchange (IX) plants (referred to as Plants A and B) and two activated alumina (AA) plants (referred to as Plants C and D), with capacities varying from 800 to 3,000 gallons per day (gpd). The objective of sampling and analysis was to evaluate the performance of the full-scale water treatment plants to consistently remove arsenic from source water. Additionally, data were collected to evaluate the chemical characteristics of residuals produced by these treatment processes.

The study was divided into three phases: source water sampling, preliminary sampling, and long-term evaluation. Source water sampling was conducted to evaluate source water characteristics at each plant. Preliminary sampling was initiated in August 1998 and consisted of four sampling events conducted at each facility on either a weekly or biweekly basis to refine procedures for subsequent events during the third phase. Long-term evaluation consisted of weekly or biweekly sampling at each facility from September 1998 to September 1999.

Samples from resin regeneration were collected at Plant A from March to June 1999. Spent AA samples were collected at Plants C and D during the media change-out events in December 1998 and May 1999, respectively. Results from the long-term evaluation demonstrated that both the IX and AA systems are capable of achieving arsenic levels of less than 5 µg/L in the treated water, provided that the IX resin was regenerated or the AA medium was changed out before arsenic breakthrough occurred. The two IX systems had inlet arsenic concentrations between 45 and 65 µg/L [primarily As(V)]. When Plant A was operated beyond 3,000 to 3,200 bed volumes (BV) of water, arsenic chromatographic peaking occurred. Arsenic breakthrough was not observed at Plant B where an average 97% of removal efficiency was achieved, leaving only 0.8 to 4.5 µg/L arsenic in the finished water.

Both AA systems consisted of two parallel treatment trains with a roughing AA column followed by a polishing column in each train. The systems operated on a media throwaway basis. The average arsenic removal efficiencies achieved at Plants C and D were 87% and 98%, respectively. The raw water at Plant C (34 to 76 µg/L total arsenic) contained approximately 0.3 to 28.8 µg/L As(III), which was nearly completely removed, even though no oxidation treatment was provided. The water at Plant D contained slightly higher total arsenic concentrations (53.3 to 87 µg/L) but no As(III), which was consistently removed to less than 5 µg/L in the finished water.

The AA media in the roughing tanks were exhausted and disposed of about every 1 to 1.5 years after treating approximately 9,600 BV at Plant C and 5,260 BV at Plant D. The regeneration process at Plant A recovered from 67 to 86% of arsenic from the spent brine. The spent AA at Plants C and D passed the Toxicity Characteristic Leaching Procedure (TCLP) test for metals including arsenic, and therefore was disposed of as nonhazardous waste.

Laboratory Study on the Oxidation of Arsenic III to Arsenic V

EPA 600-R-01-021

A one-year laboratory study was performed to determine the ability of seven oxidants to oxidize As(III) to As(V). These included chlorine, permanganate, ozone, chlorine dioxide, monochloramine, a solid-phase oxidizing media, and 254 nm ultraviolet light. Chlorine and permanganate rapidly oxidized As(III) to As(V) in the pH range of 6.3 to 8.3. Dissolved manganese, dissolved iron, sulfide and TOC slowed the rate of oxidation slightly, but essentially complete oxidation was obtained in less than one minute with chlorine and permanganate under all conditions studied.

In the absence of interfering reductants, ozone rapidly oxidized As(III). Although, dissolved manganese and dissolved iron had no significant effect on As(III) oxidation, the presence of sulfide considerably slowed the oxidation reaction. The presence of TOC had a quenching effect on As(III) oxidation by ozone, producing incomplete oxidation at the higher TOC concentration studied. Only limited As(III) oxidation was obtained using chlorine dioxide, which was probably due to the presence of chlorine (as a by-product) in the chlorine dioxide stock solutions. The reason for the ineffectiveness of chlorine dioxide was not studied.

Preformed monochloramine was ineffective for As(III) oxidation, whereas limited oxidation was obtained when monochloramine was formed in-situ. This showed that the injected chlorine probably reacted with As(III) before being quenched by ammonia to form monochloramine. Filox, a manganese dioxide-based media, was effective for As(III) oxidation.

When dissolved oxygen (DO) was not limiting, complete oxidation was observed under all conditions studied. However, when DO was reduced, incomplete oxidation was obtained in the presence of interfering reductants. The adverse effect of interfering reductants was completely eliminated by either (a) supplying enough DO or (b) increasing the contact time. In addition to oxidizing As(III), the Filox media also removed some arsenic by adsorption, which diminished greatly as the media came into equilibrium with the As(III)-spiked synthetic water.

UV light alone (254 nm) was not very effective for As(III) oxidation. Significant oxidation was observed only at very low flow rates representing 0.6 - 2.5% of the rated capacities of the two UV sterilizer units tested. However, as reported in a patented process, complete oxidation by UV light was observed when the challenge water was spiked with 1.0 mg/L sulfite.

Treatment of Arsenic Residuals from Drinking Water Removal Processes

EPA 600-R-01-033

The drinking water MCL was recently lowered from 0.05 mg/L to 0.01 mg/L. One concern was that a reduction in the TCLP arsenic limit in response to the drinking water MCL could be problematic with regard to disposal of solid residuals generated at arsenic removal facilities. This project focused on developing a short-list of arsenic removal options for residuals produced by ion exchange (Ion Ex), reverse osmosis (RO), nanofiltration (NF), activated alumina (AA), and iron removal processes. Both precipitation and adsorption processes were evaluated to assess their arsenic removal effectiveness.

In precipitation tests, ferric chloride outperformed alum for removal of arsenic from residuals by sedimentation, generally resulting in arsenic removals of 88 to 99 percent. Arsenic removal from the high alkalinity ion exchange samples was poorer. The required iron-to-arsenic molar ratio for best removal of arsenic in these screening tests varied widely from 4:1 to 191:1, depending on residuals type, and best arsenic removal using ferric chloride typically occurred between pH 5.0 and 6.2. Polymer addition typically did not significantly improve arsenic removal using either coagulant. Supernatant total arsenic levels of 0.08 mg/L or lower were attained with ferric chloride precipitation for membrane concentrates and residuals from iron removal facilities compared to an in-stream arsenic limit of 0.05 mg/L in place in some states.

Settling alone with no coagulant also effectively removed arsenic from iron removal facility residuals. Even with ferric chloride dosages of 50 to 200 mg/L applied to ion exchange regenerants, supernatant arsenic levels after treatment were 1 to 18 mg/L. Required iron-to-arsenic molar ratios developed in precipitation work could be used by utilities as guidelines for establishing coagulant dose needs to meet in-stream standards, and to develop preliminary treatment costs.

Adsorption tests demonstrated the potential for different types of media and resins to remove arsenic from liquid residuals, but did not assess ultimate capacity. Overall, the iron-based granular ferric hydroxide media evaluated in testing outperformed the aluminum-based media and ion exchange resin for removal of arsenic. However, activated alumina and the iron-based media provided comparable arsenic removals of close to 100 percent with an empty bed contact time (EBCT) of 3-min for most of the membrane concentrates and the settled iron removal facility residuals. Removal of suspended solids was key to the success of adsorption for spent filter backwash water and clarifier flush residuals. Arsenic breakthrough occurred very rapidly for the ion exchange samples and for one RO concentrate, all of which had an alkalinity of more than 1,000 mg/L (as CaCO₃). This again suggests that alkalinity significantly interferes with adsorption of arsenic. Based on this work, use of adsorption media for treatment of arsenic-laden water plant residuals merits further exploration.

Of all of the residuals streams tested, Ion Ex regenerants were the most difficult to treat using precipitation or adsorption. Disposal of supernatant streams resulting from treatment of arsenic-laden residuals from ion exchange plants could pose a major challenge. TCLP arsenic levels in all residuals generated in this work and in full-scale solid media samples were far below the regulatory limit of 5 mg/L, and in fact were below 0.5 mg/L.

Oxidation of As(III) by Aeration and Storage

EPA 600-R-01-102

A study of the effects of aeration and storage on the oxidation of arsenic(III) was undertaken at three utilities in the U.S. to establish the engineering significance of aeration as a potential pre-treatment method for arsenic removal. Aeration has been referred to in the literature as a possible useful pre-treatment method to ensure that arsenic is in the arsenic(V) state before subsequent removal by any of several treatment processes. Since aeration is a common process for treating groundwater for iron oxidation, radon, volatile organics, carbon dioxide, and hydrogen sulfide, it is reasonable to investigate its effectiveness for arsenic(III) oxidation.

The results of this study clearly establish that aeration and aerobic storage do not oxidize arsenic (III). The major conclusion is that aeration is not effective for this purpose and should not be relied upon or expected to contribute to the oxidation of arsenic(III).

One of the test sites in this study clearly showed that arsenic(III) is significantly removed by the oxidation and precipitation of iron, but this should not be attributed to an oxidation of arsenic(III) to arsenic(V) by dissolved oxygen. Past research has established that iron precipitation can be partially effective for the adsorptive removal of arsenic(III), and this is the likely explanation for the apparent drop in arsenic(III) at the site that had high iron.

The effect of iron precipitation on the removal of arsenic was also present in the long term storage of aerated water in this study. When all of the iron (initial iron at 2.7 mg/L) precipitated from the quiescent storage water, the remaining aqueous total arsenic was entirely dissolved and in the arsenic (V) state.

The aqueous arsenic (III) was below detection and apparently completely removed or converted by the insoluble iron. Even in this case it is doubtful if DO was responsible for any oxidation of arsenic(III), because the loss directly correlated to the loss of iron precipitate and no other instance of arsenic(III) oxidation occurred at the other sites. In summary, the data supported the fact that iron is extremely important in the removal of arsenic(III), but did not support the idea that arsenic(III) is oxidized by aeration. This is true at least for the conditions used in this study.

While the subtleties of the results are interesting, especially for the site with high iron, it is important to emphasize the original objective of this study, which was to establish if typical aeration and storage methods could oxidize arsenic(III). Based upon the results of this study, it is concluded that aeration does not oxidize arsenic(III) and that subsequent storage for up to five days does not result in arsenic(III) oxidation. Dissolved oxygen should not be considered as a candidate for arsenic(III) oxidation; however, aeration will continue to be considered a very effective process for the oxidation of iron. In that way, aeration can be said to be effective in bringing about the removal of As via the oxidative precipitation of iron.

Design Manual: Removal of Arsenic from Drinking Water by Adsorptive Media

EPA 600-R-03-019

This design manual is an in-depth presentation of the steps required to design and operate a water treatment plant for removal of excess arsenic from drinking water using the adsorptive media process. This treatment process is very reliable, simple and cost-effective. Several adsorptive media products are available in the market-place that have successfully demonstrated their capability to remove arsenic from drinking water to levels well below the revised MCL, 0.010 mg/L. Other new products continue to be developed. The adsorptive media products are preferential for the removal of arsenic over other competing ions. Therefore, unless a water system requires treatment capability for removal of other suspended or dissolved contaminants, the adsorptive media treatment method merits evaluation.

The adsorptive media process is implemented with operational options which vary with the product selected. For water systems that are primarily concerned with financial feasibility, capital and operating costs, each operational option along with each available adsorptive media product should be evaluated. This design manual provides the methods for competently performing each evaluation. The arsenic removal capacity of some adsorptive media products, such as activated alumina, are very sensitive to the pH of the water passing thru treatment. Others, such as iron-based products, are not. Treatment processes incorporating pH adjustment capability require careful handling and storage of corrosive chemicals (acid and caustic). Some adsorptive media products, such as activated alumina, are capable of being chemically regenerated for repetition of treatment cycles using the same corrosive chemicals as those used for pH adjustment in the treatment process.

Regeneration is not recommended for other adsorptive media products. Whether or not pH of water being treated is adjusted, the adsorptive media can be replaced in place of regeneration upon exhaustion of arsenic capacity. This design manual presents the information necessary to design and operate treatment systems for any combination of operational options and for any adsorptive media. It also discusses the capital and operating costs including the many variables which can raise or lower costs for identical treatment systems.

Design Manual: Removal of Arsenic from Drinking Water by Ion Exchange

EPA 600-R-03-080

This design manual is an in-depth presentation of the steps required to design and operate a water treatment plant for removing arsenic in the As(V) form from drinking water using the anion exchange process. Because As(III) occurs as an uncharged anion in ground water in the pH range of 6.5 to 8, the process will not remove As(III) unless it is first oxidized to As(V). The manual also discusses the capital and operating costs, including many of the variables that can raise or lower costs for identical treatment systems.

The anion exchange treatment process is very reliable, simple, and cost-effective. The treatment process removes arsenic using a strong base anion exchange resin in either the chloride or hydroxide form, with chloride the preferred form because salt can be used as the regenerant. The process preferentially removes sulfate over arsenic; and, therefore, as the sulfate increases in the raw water, the process becomes less efficient and more costly.

Furthermore, because sulfate occurs in significantly higher concentrations than arsenic, treatment run lengths are dependent almost entirely on the sulfate concentration of the raw water. The ion exchange process is a proven efficient and cost-effective treatment method for removing As(V) from water supplies with low sulfate levels.

The configuration of an anion exchange system for As(V) removal can take several forms. The method presented in this design manual uses three vertical cylindrical pressure vessels operating in a downflow mode. Two of the three treatment vessels are piped in parallel to form the primary arsenic removal stage. The third treatment vessel is piped in series in the lag position. In the primary stage, raw water flows through one of the two treatment vessels while the second vessel is held in the standby position. When the treatment capacity of the first vessel approaches exhaustion, it is removed from service and replaced by the second primary stage vessel. While out of service, the first vessel is regenerated and placed in the standby position. The role of the third treatment vessel in the lag position is to ensure that any arsenic that breaks (peaking) through one of the lead vessels does not enter the distribution system. Although this design concept results in higher capital costs, it prevents high arsenic concentrations in the treated water, if operated properly.

Capital Costs of Arsenic Removal Technologies Demonstration Program Round 1

EPA 600-R-04-201

On January 18, 2001, the U.S. Environmental Protection Agency (EPA) finalized the maximum contaminant level (MCL) for arsenic at 0.01 mg/L. EPA subsequently revised the rule text to express the MCL as 0.010 mg/L (10 µg/L). The final rule requires all community and non-transient, non-community water systems to comply with the new standard by February 2006. In October 2001, the EPA announced an initiative for additional research and development of cost-effective technologies to help small community water systems (<10,000 customers) meet the new arsenic standard, and to provide technical assistance to operators of small systems in order to reduce compliance costs.

As part of this Arsenic Rule Implementation Research Program, EPA's Office of Research and Development (ORD) proposed a project to conduct a series of full-scale, long-term, on-site demonstrations of arsenic removal technologies, process modifications, and engineering approaches applicable to small systems in order to evaluate the efficiency and effectiveness of arsenic removal systems at meeting the new arsenic MCL. For the Round 1 demonstration study, the selected arsenic treatment technologies include nine adsorptive media systems, one ion exchange system, one coagulation/filtration system, and one process modification. The adsorptive media systems use four different adsorptive media, including three iron-based media, i.e., ADI's G2, Severn Trent and AdEdge's E33, and USFilter's GFH, and one iron-modified activated alumina media, i.e., Kinetico's AAFS50 (a product of Alcan). Since the inception of the project, 10 of 12 systems have been installed, with flowrates at all systems ranging from 37 to 640 gpm.

A key objective of the long-term demonstration project is to determine the cost-effectiveness of the technologies. This report provides a brief description of each of the 12 Round 1 demonstration sites and the respective technologies being evaluated.

Capital costs were organized into three categories— equipment, engineering, and installation— and then summed to arrive at a total capital investment cost for each system. Operations and

maintenance (O&M) costs associated with the treatment systems are not yet available; however, vendor-supplied estimates on media replacement costs also are provided in this report.

Excluding the cost for one system modification site, the total capital investment costs range from \$90,757 to \$305,000, and vary by flowrate, system design, material of construction, monitoring equipment, and specific site conditions. Based on a 3% interest rate and a 20-year return period, the unit costs of the total capital investment range from \$0.03 to \$0.79 per 1,000 gallons of water treated. In general, the unit cost decreases as the size of a treatment system increases. The equipment costs for the treatment systems range from \$66,235 to \$218,000, representing 54 to 80% of the total capital investment cost. Engineering costs for the treatment systems range from \$4,907 to \$50,659, accounting for 5 to 22% of the total capital investment with an average of 12%. Installation costs for the treatment systems range from \$13,150 to \$77,574, which accounts for 12 to 34% of the total capital investment with an average of 22%. Finally, building cost information obtained from the host facilities also is provided in the report. Building costs range from \$3,700 to \$186,000, varying according to differences in location, size, design, material of construction, and choice of construction contractor.

Technology Selection and System Design, USEPA Arsenic Demonstration Program Round 1

EPA 600-R-05-001

On January 18, 2001, the U.S. Environmental Protection Agency (EPA) finalized the maximum contaminant level (MCL) for arsenic at 0.01 mg/L. EPA subsequently revised the rule text to express the MCL as 0.010 mg/L (10 µg/L). The final rule requires all community and non-transient, non-community water systems to comply with the new standard by February 2006. In October 2001, EPA announced an initiative for additional research and development of cost-effective technologies to help small community water systems (<10,000 customers) meet the new arsenic standard, and to provide technical assistance to operators of small systems in order to reduce compliance costs.

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This report provides the source water quality characteristics at each of the 12 demonstration sites and the general rationale used to select the technologies for demonstration at each site. Information on the design and operation of each treatment system also is presented.

The selection of the technologies for demonstration at each location was a cooperative decision made by the water system, state, and EPA. Many factors were considered in the selection process, including water quality, residual production and disposal, complexity of system

operation, and costs. The selection of the adsorptive media and pretreatment methods depended on a number of factors that affect the system performance, including arsenic concentration and speciation, pH, and the presence of competing anions, as well as media-specific characteristics such as costs, media life, and empty-bed contact time (EBCT) requirements.

Using DWSRF Funds to Comply with the New Arsenic Rule

EPA 816-F-02-004

The Drinking Water State Revolving Fund (DWSRF) program was established by the 1996 Safe Drinking Water Act (SDWA) Amendments and authorizes grants to states to capitalize revolving loan funds. The states provide low-interest loans to eligible systems for infrastructure improvements needed to ensure compliance with the SDWA and protect public health. The DWSRF program can play a significant role in helping systems, especially small systems, to meet the challenges of complying with new drinking water standards.

The Environmental Protection Agency (EPA) published revisions to the Arsenic Rule in 2001 which further reduce exposure to arsenic in drinking water by adopting a new arsenic maximum contaminant level (MCL) of 10 ppb. The new MCL will impose a financial burden on some water systems. The DWSRF can provide assistance to systems to help ease this burden, increase compliance, and protect public health.

Rural Development-Rural Utilities Service, Loan, and Grant Program: Fact Sheet

EPA 816-F-03-009

USDA/Rural Development/Rural Utilities Service (RUS) administers water and wastewater loan and grant programs to improve the quality of life and promote economic development in Rural America. These programs were previously administered by the Farmers Home Administration (FmHA)

Implementation Guidance for the Arsenic Rule - Drinking Water Regulations for Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring

EPA 816-K-02-018

The final Implementation Guidance for the Arsenic Rule is based on the final rule published in the Federal Register on January 22, 2001. It incorporates comments received on the previous draft implementation guidances, and from the training sessions on the arsenic rule held throughout the country. The guidance summarizes key sections of the Proposed Rule and provides a "how to approach" for EPA Regions and States to implement the regulation. It contains an explanation of the rule's requirements and guidance for preparing State primacy revision applications. The document incorporates comments received from Regions, States, technical assistance providers, water systems, and others.

Complying With the Revised Drinking Water Standard for Arsenic: Small Entity Compliance Guide

EPA 816-R-02-008A

This guide is designed for owners and operators of community water systems (CWSs) and non-transient non-community water systems (NTNCWSs) serving 10,000 or fewer persons. CWSs include all systems (regardless of ownership) serving at least 25 year-round residents or 15 year-round service connections. NTNCWSs include all systems (regardless of ownership) that are not CWSs and that regularly serve at least 25 of the same people for more than 6 months a year. Systems that will typically find this guide useful include:

- Small towns
- Rural water districts
- Tribal systems
- Mobile home parks
- Home owners associations

Wastewater Priory Pollutants Section

Since Arsenic is a priory Pollutant.



Wastewater/Pretreatment Sampling General Information

In accordance with the Clean Water Act and General Pretreatment Program Regulations, the POTW conducts a variety of sampling activities which must be closely coordinated.

Each of these activities is briefly described below.

Permit Application Policy Example

All industrial users that require a permit must be sampled to determine the characteristics of the wastes to be discharged into the POTW's sewer system. Prior to the issuance of a permit for existing industrial users, the POTW samples the user's effluent, and performs the analyses required by the applicable discharge standards (i.e., Categorical standards or local limits).



For new industrial users, estimates of the wastes to be discharged into the POTW's sewer system must be submitted along with the permit application.

No sampling would be performed at these new facilities, since they do not presently discharge wastes into the sewer system. A four-day sampling program is usually conducted at each site to collect both composite and grab (for pollutants not amenable to composite sampling) samples as needed.

Sewer System Evaluation Policy Example

On a regular basis, selected locations in the sewer system are sampled to develop background data for purposes of updating the local limits, and to screen areas for higher than **"background"** pollutant levels. In addition, problem areas are sampled on an as needed basis to determine potential sources of POTW Code violations that either occur on a frequent basis, or are the result of a slug load to the sewer system. To monitor sewers for background information, the sampling program would typically be conducted over a four-day period. In instances where the intent is to determine sources of pollutants and/or slug loads, the length of the program would vary.

Multi-City Users (Metering Stations) Policy Example

All wastewater, which is transported to the POTW Treatment Plant from the Multi-City users, is analyzed for pollutants of concern to the Industrial Pretreatment Program. The sampling program is conducted over a five-day period to obtain four days of sampling data at each sewer location (i.e., a metering station) on a quarterly basis. Once the sampling dates have been determined, the Water Quality Inspector will notify, in writing, the Sub-regional Organizational Group (SROG) or equivalent representative for that City of the dates when the sampling will be conducted.

Sampling Safety Policy Example

Upon arrival at the site, safety is the priority. A visual inspection must be completed prior to any entry. The site must be free of any obstructions or hazards which may cause injury when entering sampling area. If there are any problems detected, the SROG or equivalent representative and the Water Quality Inspector should be notified, and no entry should be attempted until the problem has been corrected.

Metering and Sampling Stations Qualify As Confined Spaces

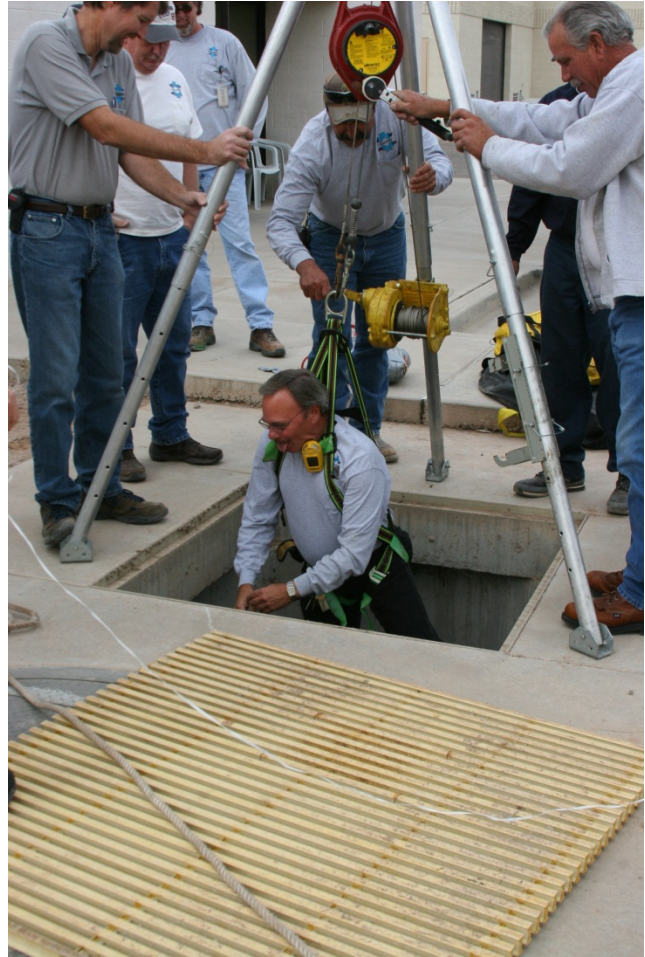
If all safety criteria have been met, prepare equipment for the site. Check the assignment sheet to determine what parameters are required to be sampled, which in turn determines the type of tubing to be used, (i.e. Tygon or Teflon).

The sampler must be completely assembled before performing QA/QC procedures. After QA/QC is complete, a sufficient amount of weight must be attached to the tubing to keep the strainer submerged in the effluent for proper siphoning of the sample, without allowing the strainer to hit the bottom of the flume. Make sure the intake tubing does not kink the metering station has a flow meter, you may connect either their cable or a POTW cable to the sampler from the flow meter. Occasionally, you will set up a flow meter to have a comparison reading. Determine the pulse rate and proper setting from the flow, and program the sampler. After entering the data into the sampler, wait to make sure the equipment is pulling samples. After the initial set-up of the sampling equipment, samples will be collected during the remainder of the sampling period. Split samples may be requested by the SROG or equivalent representative. If the volume of the sample is adequate, these may be given, provided the representative supplies the containers and allows the POTW Inspector to pour off the samples.

Upon exiting the confined space, continue to follow the confined space entry procedures as outlined by OSHA Standards. When you return to the sampling vehicle, you must immediately perform field tests and preserve the samples according to the techniques set forth in by Standard Methods or the State/Federal Rule.

All paper work must be filled out completely before the sampling crew's departure. This paperwork includes the chain of custody which is turned in to the laboratory with the samples, **"Metering Station Field Observation Form"** or equivalent form that remains with the sampling site file, and the Multi-City Metering Station Sample Record of which the original is given to the Water Quality Inspector and the copy is given to the SROG or equivalent representative. If there is not a representative at the site, these copies will be turned over to the Water Quality Inspector with the originals at the end of the week.

Remember, all paperwork should be completed prior to leaving site.



List of WWT/Pretreatment Acronyms used in this Course

Acronym Full Phrase

AA	Approval Authority
AO	Administrative Order
BAT	Best Available Technology Economically Achievable
BCT	Best Conventional Pollutant Control Technology
BMP	Best Management Practices
BMR	Baseline Monitoring Report
BOD5	5-day Biochemical Oxygen Demand
BPJ	Best Professional Judgment
BPT	Best Practicable Control Technology Currently Available
CA	Control Authority
CFR	Code of Federal Regulations
CIU	Categorical Industrial User
CSO	Combined Sewer Overflow
CWA	Clean Water Act (formerly referred to as the Federal Water Pollution Control Act or Federal Water Pollution Control Act Amendments of 1972) Pub. L. 92-500, as amended by Pub. L. 95-217, Pub. L. 95-576, Pub. L. 96-483, Pub. L. 97-117, and Pub. L. 100-4, 33 U.S.C. 1251 et seq.
CWF	Combined Wastestream Formula
CWT	Centralized Waste Treater
DMR	Discharge Monitoring Report
DSE	Domestic Sewage Exclusion
DSS	Domestic Sewage Study
ELG	Effluent Limitations Guideline
EPA	Environmental Protection Agency
EPCRA	Emergency Preparedness and Community Right to Know Act
ERP	Enforcement Response Plan
FDF	Fundamentally Different Factors
FR	Federal Register
FWA	Flow Weighted Average
GPD	Gallons per Day
IU	Industrial User
LEL	Lower Explosive Limit
MAHL	Maximum Allowable Headworks Loading
MAIL	Maximum Allowable Industrial Loading
MGD	Million Gallons per Day
MSDS	Material Safety Data Sheet
NAICS	North American Industry Classification System (replaces SIC coding in 1998)
NOV	Notice of Violation
NPDES	National Pollutant Discharge Elimination System
NRDC	Natural Resources Defense Council
NSPS	New Source Performance Standard
O&G	Oil and Grease

O&M	Operations and Maintenance
OCPSF	Organic Chemicals, Plastics, and Synthetic Fibers
P2	Pollution Prevention
PCI	Pretreatment Compliance Inspection
PCS	Permit Compliance System
PIRT	Pretreatment Implementation Review Task Force
POTW	Publicly Owned Treatment Works
PSES	Pretreatment Standards for Existing Sources
PSNS	Pretreatment Standards for New Sources
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
SIC	Standard Industrial Classification
SIU	Significant Industrial User
SPCC	Spill Prevention Control and Countermeasures
SNC	Significant Noncompliance
SSO	Sanitary Sewer Overflow
SUO	Sewer Use Ordinance
TCLP	Toxicity Characteristic Leaching Procedure
TIE	Toxicity Identification Evaluation
TOMP	Toxic Organic Management Program
TRE	Toxicity Reduction Evaluation
TRI	Toxic Release Inventory
TSS	Total Suspended Solids
TTO	Total Toxic Organics
USC	United States Code
UST	Underground Storage Tank
WET	Whole Effluent Toxicity
WWTP	Wastewater Treatment Plant



The National Pretreatment Program is unique in that the General Pretreatment Regulations require all large POTWs (i.e., those designed to treat flows of more than 5 million gallons per day) and smaller POTWs with significant industrial discharges to establish local pretreatment programs. These local programs must enforce all national pretreatment standards and requirements in addition to any more stringent local requirements necessary to protect site-specific conditions at the POTW.

Wastewater Priority Pollutants

The concentrations of various substances in water in dissolved, colloidal or suspended form are typically low but vary considerably. Priority Pollutants refer to a list of 126 specific pollutants that includes heavy metals and specific organic chemicals. The priority pollutants are a subset of "toxic pollutants" as defined in the Clean Water Act (USA). These 126 pollutants were assigned a high priority for development of water quality criteria and effluent limitation guidelines because they are frequently found in wastewater.

Each POTW with an approved pretreatment program must develop local limits for arsenic, cadmium, chromium, copper, cyanide, lead, mercury, nickel, silver and zinc or demonstrate that limits are not necessary for these pollutants. The POTW must also identify all other pollutants of concern and evaluate the need for limits for these pollutants. A pollutant of concern is defined as any pollutant limited in the POTW's NPDES permit or found in the collection system in sufficient quantity to have a reasonable potential to cause pass through or interference at the treatment plant, pose a threat to worker health and safety, or to cause other problems within the collection system or at the treatment plant, such as explosions or obstruction of wastewater flow. The priority pollutant scans performed periodically by POTWs with approved pretreatment programs are useful in identifying pollutants of concern. POTWs with multiple plants may wish to develop local limits for each plant or after calculating the limits for each plant choose the most stringent as uniform local limits across all plants.

Local limits are most often associated with the control of toxic pollutants. However, if a POTW has experienced violations of their NPDES permit effluent limits for conventional pollutants (such as BOD, TSS, ammonia, phosphorus, or oil and grease), or has experienced operational problems due to these pollutants, the POTW should investigate the need for local limits for conventional pollutants as well.

Many POTWs have surcharge programs for conventional pollutants. A surcharge program should not be confused with local limits for these pollutants. In addition to a surcharge program, which is generally triggered by specific pollutant concentrations, a POTW should set absolute upper limits for conventional pollutants in its sewer use ordinance (SUO) or industrial user (IU) permits, based on total plant capacity.

Nutrients: Carbon, nitrogen and phosphorus are substances that are excreted by humans and thus found in wastewater. Excess nutrients can stimulate the growth of algae and other aquatic plants. When these plants die and decompose, they may reduce the amount of oxygen in the water. This condition, called hypoxia, can affect the survival of fish and other aquatic organisms. Nutrients can also get into wastewater from industrial discharges, common household detergents and cleaners, runoff from streets and lawns and air pollutants that fall to the ground. Treatment plants cannot remove all nutrients from the wastewater. They can be reduced by controlling pollution that comes from lawns, farmland, streets and construction sites.

Many of the heavy metals, pesticides, and other chemicals listed here are on the priority pollutant list:

- Heavy Metals (Total and Dissolved): "Heavy Metal" in the water treatment field refers to heavy, dense, metallic elements that occur only at trace levels in water, but are very toxic and tend to accumulate.
 - o Arsenic
 - o Cadmium
 - o Chromium
 - o Lead in industry or in households
 - o Mercury
 - o Zinc
- Pesticides: Pesticides comprise a large class of compounds of concern. Typical pesticides and herbicides include DDT, Aldrin, Chlordane, Endosulfan, Endrin, Heptachlor, and Diazinon. Surprisingly, concentrations of pesticides in urban runoff may be equal or greater than the pesticides in agricultural runoff.
- Polycyclic Aromatic Hydrocarbons (PAHs): Polycyclic Aromatic Hydrocarbons include a family of semi-volatile organic pollutants such as naphthalene, anthracene, pyrene, and benzo(a)pyrene. There are typically two main sources of PAHs: spilled or released petroleum products (from oil spills or discharge of oil production brines) and combustion products that are found in urban runoff.
- Polychlorinated biphenyls (PCBs): Polychlorinated biphenyls are organic chemicals that formerly had widespread use in electrical transformers and hydraulic equipment. This class of chemicals is extremely persistent in the environment and has been proven to bioconcentrate in the food chain, thereby leading to environmental and human health concerns in areas such as the Great Lakes.

Key features of the list of priority pollutants and its relationship to the list of toxic pollutants:

1. The Priority Pollutants are a set of chemical pollutants EPA regulates, and for which EPA has published analytical test methods.
2. The Priority Pollutant list makes the list of toxic pollutants more usable, in a practical way, for the purposes assigned to EPA by the Clean Water Act. For example, the Priority Pollutant list is more practical for testing and for regulation in that chemicals are described by their individual chemical names. The list of toxic pollutants, in contrast, contains open-ended groups of pollutants, such as "chlorinated benzenes." That group contains hundreds of compounds; there is no test for the group as a whole, nor is it practical to regulate or test for all of these compounds.

Derivation

Starting with the list of toxic pollutants, EPA used four criteria to select and prioritize specific pollutants:

1. We included all pollutants specifically named on the list of toxic pollutants;
2. There had to be a chemical standard available for the pollutant, so that testing for the pollutant could be performed;
3. The pollutant had to have been reported as found in water with a frequency of occurrence of at least 2.5%, and
4. The pollutant had to have been produced in significant quantities, as reported in Stanford Research Institute's 1976 Directory of Chemical Producers, USA.

Number of Entries

Originally, there were 129. When three pollutants were removed from the list of toxic pollutants in 1981 they were also removed from the Priority Pollutant list.

1. Entry numbers 17, 49, and 50 were removed.
2. The last number on the list is still 129, although there are 126 entries.

Publication

Why is the Priority Pollutant list published at 40 CFR 423, Appendix A, rather than at section 401, or some other, more general section?

1. One of the first industrial categories for which EPA developed effluent regulations was the Steam Electric Power Generating Point Source Category. The Priority Pollutant list was included to support regulations for that category.
2. Although the other sections within part 423 apply only to Steam Electric Power Generating, the Priority Pollutant list in Appendix A is not limited in terms of its relevance to that one industrial category.
3. Some users find it helpful to think of Appendix A to Part 423 as a convenient storage place for the list, or as a matter of convenience for citation.

List of Wastewater Toxic Pollutants

Priority pollutants are a set of chemical pollutants we regulate, and for which we have developed analytical test methods. The current list of 126 Priority Pollutants, shown below, can also be found in Appendix A to 40 CFR Part 423.

- | | |
|--------------------------------|----------------------------------|
| 1. Acenaphthene | 30. 1,2-trans-dichloroethylene |
| 2. Acrolein | 31. 2,4-dichlorophenol |
| 3. Acrylonitrile | 32. 1,2-dichloropropane |
| 4. Benzene | 33. 1,2-dichloropropylene |
| 5. Benzidine | 34. 2,4-dimethylphenol |
| 6. Carbon tetrachloride | 35. 2,4-dinitrotoluene |
| 7. Chlorobenzene | 36. 2,6-dinitrotoluene |
| 8. 1,2,4-trichlorobenzene | 37. 1,2-diphenylhydrazine |
| 9. Hexachlorobenzene | 38. Ethylbenzene |
| 10. 1,2-dichloroethane | 39. Fluoranthene |
| 11. 1,1,1-trichloroethane | 40. 4-chlorophenyl phenyl ether |
| 12. Hexachloroethane | 41. 4-bromophenyl phenyl ether |
| 13. 1,1-dichloroethane | 42. Bis(2-chloroisopropyl) ether |
| 14. 1,1,2-trichloroethane | 43. Bis(2-chloroethoxy) methane |
| 15. 1,1,2,2-tetrachloroethane | 44. Methylene chloride |
| 16. Chloroethane | 45. Methyl chloride |
| 17. REMOVED | 46. Methyl bromide |
| 18. Bis(2-chloroethyl) ether | 47. Bromoform |
| 19. 2-chloroethyl vinyl ethers | 48. Dichlorobromomethane |
| 20. 2-chloronaphthalene | 49. REMOVED |
| 21. 2,4,6-trichlorophenol | 50. REMOVED |
| 22. Parachlorometa cresol | 51. Chlorodibromomethane |
| 23. Chloroform | 52. Hexachlorobutadiene |
| 24. 2-chlorophenol | 53. Hexachlorocyclopentadiene |
| 25. 1,2-dichlorobenzene | 54. Isophorone |
| 26. 1,3-dichlorobenzene | 55. Naphthalene |
| 27. 1,4-dichlorobenzene | 56. Nitrobenzene |
| 28. 3,3-dichlorobenzidine | 57. 2-nitrophenol |
| 29. 1,1-dichloroethylene | 58. 4-nitrophenol |

59.	2,4-dinitrophenol	95.	Alpha-endosulfan
60.	4,6-dinitro-o-cresol	96.	Beta-endosulfan
61.	N-nitrosodimethylamine	97.	Endosulfan sulfate
62.	N-nitrosodiphenylamine	98.	Endrin
63.	N-nitrosodi-n-propylamine	99.	Endrin aldehyde
64.	Pentachlorophenol	100.	Heptachlor
65.	Phenol	101.	Heptachlor epoxide
66.	Bis(2-ethylhexyl) phthalate	102.	Alpha-BHC
67.	Butyl benzyl phthalate	103.	Beta-BHC
68.	Di-N-Butyl Phthalate	104.	Gamma-BHC
69.	Di-n-octyl phthalate	105.	Delta-BHC
70.	Diethyl Phthalate	106.	PCB-1242 (Arochlor 1242)
71.	Dimethyl phthalate	107.	PCB-1254 (Arochlor 1254)
72.	benzo(a) anthracene	108.	PCB-1221 (Arochlor 1221)
73.	Benzo(a)pyrene	109.	PCB-1232 (Arochlor 1232)
74.	Benzo(b) fluoranthene	110.	PCB-1248 (Arochlor 1248)
75.	Benzo(k) fluoranthene	111.	PCB-1260 (Arochlor 1260)
76.	Chrysene	112.	PCB-1016 (Arochlor 1016)
77.	Acenaphthylene	113.	Toxaphene
78.	Anthracene	114.	Antimony
79.	Benzo(ghi) perylene	115.	Arsenic
80.	Fluorene	116.	Asbestos
81.	Phenanthrene	117.	Beryllium
82.	Dibenzo(h) anthracene	118.	Cadmium
83.	Indeno (1,2,3-cd) pyrene	119.	Chromium
84.	Pyrene	120.	Copper
85.	Tetrachloroethylene	121.	Cyanide, Total
86.	Toluene	122.	Lead
87.	Trichloroethylene	123.	Mercury
88.	Vinyl chloride	124.	Nickel
89.	Aldrin	125.	Selenium
90.	Dieldrin	126.	Silver
91.	Chlordane	127.	Thallium
92.	4,4-DDT	128.	Zinc
93.	4,4-DDE	129.	2,3,7,8-TCDD
94.	4,4-DDD		

Types of POTW's Wastewater Samples

General

There are four types of samples that are collected by the POTW's Sampling Section: grab, time proportional composites, flow proportional composites, and hand composites. The sampling method used depends largely on the types of analyses to be run, and the nature of the wastestream being sampled. Each sampling method is described in this section.

Most POTW's will define the sampling methods which must be used by industrial users (IUs) to obtain representative samples to show compliance with their permits: **Example**

- (1) A grab sample is an individual sample collected in less than 15 minutes without regard for flow or time of day. pH, cyanide, oil and grease, sulfide, and volatile organics must be collected as grab samples.
- (2) 24-hour flow proportional composite samples where feasible. The POTW may waive this requirement if the IU demonstrates that this method is not feasible. Samples would then be taken by means of time proportional composite sampling methods or by hand composite where the industrial User (IU) can demonstrate that this will provide a representative sample of the effluent being discharged.

The volume of sample to be collected by any of these methods is dependent on the number and types of analyses that must be performed.

Wastewater Grab Samples

Grab samples are individual samples collected in less than 15 minutes without regard to flow or time of day. Grab samples are normally taken manually, but can be pumped. Oil and grease samples and purgeable organics are exceptions and must be taken manually.



A grab sample is usually taken when a sample is needed to:

- (1) Provide information about an instantaneous concentration of pollutants at a specific time.
- (2) Quantify the pollutants in a non-continuous discharge (e.g., batch discharge).
- (3) Corroborate composite samples if the waste is not highly variable.
- (4) Monitor parameters not amenable to compositing such as pH, temperature, dissolved oxygen, chlorine, purgeable organics and sulfides, oil and grease, coliform bacteria, and sulfites.



The Refrigerated Automatic Sampler will have a Data programmer that will allow you to set the time to collect the sample or samples. This machine can also measure the amount of the sample. These can also be used for the collection of composite samples. Sometimes you will see a pH probe with real-time readings sent to the Operator's Command Center. This is a common sight for most wastewater plants and SIUs.



Collecting Procedure for Water/Wastewater Grab Samples

Policy Example

Lower dipper or mouth of the bottle into water just below surface. In some cases, you will need to rinse the bottle or dipper three times in the sample before obtaining the sample.

Retrieve collected sample to clean processing area.

Rinse the outside of the bottle 3 times to remove contamination.

Pour the sample into the required laboratory bottle.

You may need to filter the sample, this is true with some water and wastewater samples.

Filtering (for ortho-P and NO_x samples). Some surface water virus samples need to be filtered.

- Secure caps tightly.
- Bottle preservation is performed in the truck or lab before sampling.
- Secure sample container caps tightly.
- Label the sample containers and place them in an iced cooler before storage.

Timed Composites

Timed samples are usually taken in instances where the intention is to characterize the wastes over a period of time without regard to flow, or where the flow is fairly constant. Timed composite samples consist of a series of equal volume grab samples taken at regular intervals. Usually the interval is 15 minutes with a maximum sampling duration of 24 hours.

However, other intervals can be used and may be more appropriate under some circumstances. Samplers are available which can take up to 10 discrete samples per bottle, for a total of 240 discrete samples. The sampler may be programmed to take any number of samples into one composite bottle which has a 2.5-gallon capacity.

Flow Proportional Composites

Flow proportional composite samples consist of: a series of grab samples whose volumes are equal in size and proportion to the flow at the time of sampling. Samples are taken at varying time intervals, or continuous samples taken over a period of time based on the flow. Wherever possible, flow proportional sampling is recommended because it most accurately reflects the nature of the wastestream. Equal volume samples taken at varying time intervals are most often collected by the sampling inspectors. A flow measuring device should be used in conjunction with the automatic sampler.

This sampling method is used for all sampling activities except for instances where grab samples are required or time proportional sampling is more expedient and can provide the same accuracy as flow proportional sampling (i.e., constant flow levels).

Hand Compositing

Hand compositing is a series of time proportional grab samples which are collected and composited by hand. Provided the sample volumes are equal and are collected at even intervals, the results should be the same as if done by an automatic sampler (i.e., flow proportional composite sampling).

A specific instance where this sampling method may be used is in metal plating shops which have batch discharges from the treatment tank. Provided the tank contains a homogeneous mixture, a minimum of four grab samples are taken of equal amounts and at evenly spaced intervals of time during discharge, to accurately represent the entire tank.

This should represent the waste characteristics of the entire batch discharged to the sewer. One hand composite per batch discharged would be equivalent to a 24-hour composite sample taken at other types of facilities. The sampling data would be compared with the average daily categorical standards or local limits where applicable.



Parshall Fume and Ultrasonic Flow Meter
Notice the debris and most POTW's will write a NOV for uncleanness.



Proper Sample Handling

The proper handling of water quality samples also includes wearing gloves. Gloves not only protect field personnel, but also prevent potential contamination to the water sample. Always wear powderless, disposable gloves. When sampling for inorganics, wear latex gloves. Nitrile gloves are appropriate for organics.

The following sections provide a field reference for chain of custody procedures, sampling surface water and ground water, and further provides procedures for measuring field parameters and handling water-quality samples.

Use chain-of-custody procedures when coolers and containers are prepared, sealed and shipped. They will remain sealed until used in the field. When making arrangements with the laboratory, make sure you request enough containers, including those for blank and duplicate samples. Order extra sample bottles to allow for breakage or contamination in the field.



Some samples require low-temperature storage and/or preservation with chemicals to maintain their integrity during shipment and before analysis in the laboratory. The most common preservatives are hydrochloric, nitric, sulfuric and ascorbic acids, sodium hydroxide, sodium thiosulfate, and biocides. Many laboratories provide pre-preserved bottles filled with measured amounts of preservatives. Although most federal and state agencies allow the use of pre-preserved sample containers, some may require either cool temperatures or added preservatives in the field.

When the containers and preservatives are received from the laboratory, check to see that none have leaked. Be aware that many preservatives can burn eyes and skin, and must be handled carefully. Sampling bottles should be labeled with type of preservative used, type of analysis to be done and be accompanied by a Material Safety Data Sheet (**MSDS**).

Make sure you can tell which containers are pre-preserved, because extra care must be taken not to overfill them when collecting samples in the field. Check with the laboratory about quality control procedures when using pre-preserved bottles. Coolers used for sample shipment must be large enough to store containers, packing materials and ice. Obtain extra coolers, if necessary. Never store coolers and containers near solvents, fuels or other sources of contamination or combustion. In warm weather, keep coolers and samples in the shade.

Field Parameters

Measure and record the field parameters of temperature, electrical conductivity, pH and dissolved oxygen in an undisturbed section of streamflow. Other parameters may be measured, if desired.

QA/QC Field Procedures for Plant Sampling *Example*

Duplicate Sampling Procedure

The purpose of Duplicate Samples is to check the laboratory's ability to reproduce analytical results. Duplicate Samples are to be collected using these steps:

1. Determine amount of sample needed. If a flow proportion sample is required, then base the amount of sample needed on the current flow reading. If a flow-proportion sample is not required, then use the predetermined amount for the sampling site.
2. Collect sample using a grab type sampler or a sampling head.
3. Measure the amount determined in Step 1 using a graduated cylinder or other accurate measuring device.
4. Pour measured sample into sample container that is not marked as the Duplicate Sample.
5. Measure same amount as in Step 1
6. Pour second measured quantity into sample container marked for Duplicate Sample.
7. Process both samples using standard procedures and submit both samples to laboratory.

Split Sampling Procedure

The purpose of Split Samples is to check analytical procedures by having the samples analyzed by two different laboratories. Split Samples are to be collected using these steps:

1. Determine amount of sample needed. If a flow proportion sample is required, then base the amount of sample needed on the current flow reading. If a flow-proportion sample is not required, then use the predetermined amount for the sampling site.
2. Collect sample using a grab type sampler or a sampling head.
3. Measure the amount determined in Step 1 using a graduated cylinder or other accurate measuring device.
4. Pour measured sample into sample container that is not marked as the Split Sample.
5. Measure same amount as in Step 1
6. Pour second measured quantity into sample container marked for Split Sample.
7. Process both samples using standard procedures and submit both samples to the laboratory. The laboratory will be responsible for submitting the samples to the outside laboratory that will be analyzing the Split Sample.

Trip Blank Procedure

The purpose of Trip Blanks is to determine if the sample bottles have been adequately cleaned, and if sample contamination occurs between the time sample bottles leave the laboratory to the time that samples are returned to the lab. Trip blanks are prepared by the laboratory using bottles supplied by the sampler. They are picked up by the person who begins the sampling day. Trip blanks are placed in the cooler which contains the other samples and remain there until the samples are turned into the laboratory.

Sampling Techniques for Heavy Metals

- (1) Generally, all metal samples collected are to be composite samples, i.e., flow/composite, time/composite, or hand composite.
- (2) For composite sampling, place the lid on the bottle and agitate the bottle to completely mix the composite sample.
- (3) Transfer the required amount from the composite container to either a 500 ml or 2000 ml clean plastic bottle. Check the pH of the sample as described in Section 8.7.2.5.

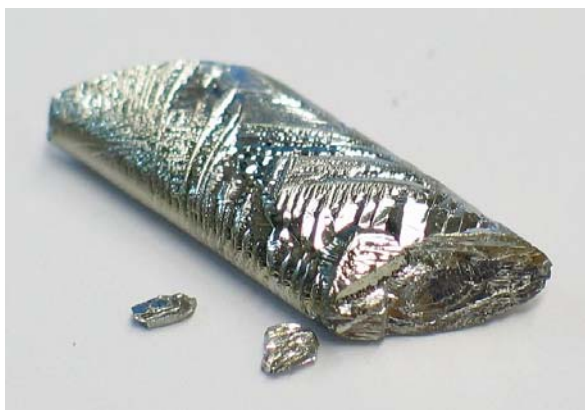
Note: For inductively coupled plasma (ICP) metal analysis, a 500 ml clean plastic bottle is required. For extra metals or metals by furnace, a 2000 ml clean plastic bottle is required.

- (4) Add nitric acid (1:1 solution) to the sample to reduce the pH to below 2.0. Usually, 2 ml/500 ml is sufficient. Recheck the pH to be sure it is below 2.0. Make a note on the lab sheet if more than two ml of acid is required to bring the pH below 2.0.
- (5) Label the sample bottle with the corresponding IW number and proper analysis code letter. Attach the custody seal to the sample, then store in the ice chest until transferred to the laboratory. Fill out the IW lab sheet with all the pertinent information, being careful to include all required parameters and the type of analysis required, e.g., ICP/furnace.
- (6) When a grab sample is necessary, rinse out the receiving sample bottle with an aliquot of the sample stream at least three times. Then fill the sample bottle and proceed with steps two through four described above.
- (7) When a split sample is requested (i.e., one for the samplers and one for the user), the composite sample is prepared as described in item one. Providing there is sufficient sample, a portion is transferred into the bottle provided by the user.
- (8) If more than one site is sampled per day, a clean composite container (i.e., two and one half-gallon glass jar), must be used at each site.
- (9) If a discreet sampler is being used, at the time of collection combine all the samples that have been collected into a single clean composite bottle. Then follow the preceding steps one through four, and refer to step six if a split is requested.

IOC Section

Periodic Table of the Elements

1 IA		New Original		Alkali metals		Actinide series		C Solid		13		14		15		16		17		18 VIIIA	
1 H Hydrogen 1.00794		2 He Helium 4.002602		Alkaline earth metals		Poor metals		Br Liquid		H Gas		III A		IV A		V A		VI A		VII A	
3 Li Lithium 6.941		4 Be Beryllium 9.012182		Transition metals		Nonmetals		H Gas		5 B Boron 10.811		6 C Carbon 12.0107		7 N Nitrogen 14.00644		8 O Oxygen 15.9994		9 F Fluorine 18.998433		10 Ne Neon 20.1797	
11 Na Sodium 22.989770		12 Mg Magnesium 24.3050		Lanthanide series		Noble gases		Tc Synthetic		13 Al Aluminum 26.981538		14 Si Silicon 28.0855		15 P Phosphorus 30.973761		16 S Sulfur 32.064		17 Cl Chlorine 35.453		18 Ar Argon 39.948	
19 K Potassium 39.0983		20 Ca Calcium 40.078		57 to 71		21 Sc Scandium 44.955910		22 Ti Titanium 47.867		23 V Vanadium 50.9415		24 Cr Chromium 51.9961		25 Mn Manganese 54.938045		26 Fe Iron 55.845		27 Co Cobalt 58.933200		28 Ni Nickel 58.6934	
37 Rb Rubidium 85.4678		38 Sr Strontium 87.62		89 to 103		39 Y Yttrium 88.90585		40 Zr Zirconium 91.224		41 Nb Niobium 92.90638		42 Mo Molybdenum 95.94		43 Tc Technetium (98)		44 Ru Ruthenium 101.07		45 Rh Rhodium 101.07		46 Pd Palladium 106.42	
55 Cs Cesium 132.90545		56 Ba Barium 137.327		57 to 71		72 Hf Hafnium 178.49		73 Ta Tantalum 180.9479		74 W Tungsten 183.84		75 Re Rhenium 186.207		76 Os Osmium 190.23		77 Ir Iridium 192.217		78 Pt Platinum 195.078		79 Au Gold 196.96655	
87 Fr Francium (223)		88 Ra Radium (226)		89 to 103		104 Rf Rutherfordium (261)		105 Db Dubnium (262)		106 Sg Seaborgium (266)		107 Bh Bohrium (264)		108 Hs Hassium (269)		109 Mt Meitnerium (268)		110 Ds Darmstadtium (271)		111 Rg Roentgenium (282)	
Atomic masses in parentheses are those of the most stable or common isotope.																					
Design Copyright © 1997 Michael Dayde mdayde@dayde.com http://www.dayde.com/periodic/																					
Note: The subgroup numbers 1-18 were adopted in 1994 by the International Union of Pure and Applied Chemistry. The names of the Latin equivalents of those numbers																					
57 La Lanthanum 138.9055		58 Ce Cerium 140.116		59 Pr Praseodymium 140.90765		60 Nd Neodymium 144.24		61 Pm Promethium (145)		62 Sm Samarium 150.36		63 Eu Europium 151.964		64 Gd Gadolinium 157.25		65 Tb Terbium 158.92534		66 Dy Dysprosium 162.500		67 Ho Holmium 164.93032	
89 Ac Actinium (227)		90 Th Thorium 232.0381		91 Pa Protactinium 231.03688		92 U Uranium 238.02891		93 Np Neptunium (237)		94 Pu Plutonium (244)		95 Am Americium (243)		96 Cm Curium (247)		97 Bk Berkelium (247)		98 Cf Californium (251)		99 Es Einsteinium (252)	
101 Md Mendelevium (258)		102 No Nobelium (259)		103 Lr Lawrencium (262)		104 Rf Rutherfordium (261)		105 Db Dubnium (262)		106 Sg Seaborgium (266)		107 Bh Bohrium (264)		108 Hs Hassium (269)		109 Mt Meitnerium (268)		110 Ds Darmstadtium (271)		111 Rg Roentgenium (282)	



Left, Tellurium, right Astatine with Fluorine



Common water sample bottles for distribution systems.

Radiochemicals, VOCs, (Volatile Organic Compounds), THMs, Total Trihalomethanes), Nitrate, Nitrite.

Most of these sample bottles will come with the preservative already inside the bottle.

Some bottles will come with a separate preservative (acid) for the field preservation.

Slowly add the acid or other preservative to the water sample; not water to the acid or preservative.

Inorganic Chemicals

Contaminant	MCLG ¹ (mg/L) ²	MCL or TT ¹ (mg/L) ²	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
Antimony	0.006	0.006	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder
Arsenic	0 ^Z	0.010 as of 01/23/06	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer	Erosion of natural deposits; runoff from orchards, runoff from glass & electronics production wastes
Asbestos (fiber >10 micrometers)	7 million fibers per liter	7 MFL	Increased risk of developing benign intestinal polyps	Decay of asbestos cement in water mains; erosion of natural deposits
Barium	2	2	Increase in blood pressure	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits
Beryllium	0.004	0.004	Intestinal lesions	Discharge from metal refineries and coal- burning factories; discharge from electrical, aerospace, and defense industries
Cadmium	0.005	0.005	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
Chromium (total)	0.1	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Copper	1.3	TT ^Z ; Action Level=1.3	Short term exposure: Gastrointestinal distress Long term exposure: Liver or	Corrosion of household plumbing systems; erosion of natural deposits

Inorganic Chemicals

Contaminant	MCLG ¹ (mg/L) ²	MCL or TT ¹ (mg/L) ²	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
			kidney damage	
			People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level	
Cyanide (as free cyanide)	0.2	0.2	Nerve damage or thyroid problems	Discharge from steel/metal factories; discharge from plastic and fertilizer factories
Fluoride	4.0	4.0	Bone disease (pain and tenderness of the bones); Children may get mottled teeth	Water additive which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminum factories
Lead	zero	TT ² ; Action Level=0.015	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities Adults: Kidney problems; high blood pressure	Corrosion of household plumbing systems; erosion of natural deposits
Mercury (inorganic)	0.002	0.002	Kidney damage	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands
Nitrate (measured as Nitrogen)	10	10	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits
Nitrite (measured as Nitrogen)	1	1	Infants below the age of six months who drink water containing nitrite in excess of	Runoff from fertilizer use; leaking from septic tanks, sewage;

Inorganic Chemicals

Contaminant	MCLG ¹ (mg/L) ²	MCL or TT ¹ (mg/L) ²	Potential Health Effects from Long-Term Exposure Above the MCL (unless specified as short-term)	Sources of Contaminant in Drinking Water
			the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue- baby syndrome.	erosion of natural deposits
Selenium	0.05	0.05	Hair or fingernail loss; numbness in fingers or toes; circulatory problems	Discharge from petroleum refineries; erosion of natural deposits; discharge from mines
Thallium	0.0005	0.002	Hair loss; changes in blood; kidney, intestine, or liver problems	Leaching from ore- processing sites; discharge from electronics, glass, and drug factories



What are Inorganic Compounds?

Inorganic compounds are of inanimate, not biological origin. Inorganic compounds lack carbon and hydrogen atoms and are synthesized by the agency of geological systems. In contrast, the synthesis of organic compounds in biological systems incorporates carbohydrates into the molecular structure. Organic chemists traditionally refer to any molecule containing carbon as an organic compound and by default this means that inorganic chemistry deals with molecules lacking carbon. However, biologists may distinguish organic from inorganic compounds in a different way that does not hinge on the presence of a carbon atom.

Pools of organic matter, for example, that have been metabolically incorporated into living tissues persist in decomposing tissues, but as molecules become oxidized into the open environment, such as atmospheric CO₂, this creates a separate pool of inorganic compounds. The distinction between inorganic and organic compounds is not always clear when dealing with open and closed systems, because everything is ultimately connected to everything else on the planet. Some scientists, for example, view the open environment (i.e., the ecosphere) as an extension of life and from this perspective may consider atmospheric CO₂ as an organic compound. IUPAC, an agency widely recognized for defining chemical terms, does not offer definitions of inorganic or organic.

Inorganic compounds are rather simple chemicals present in ground water. These chemicals are generally described as mineral in nature and usually exist as ions (chemical substances with a positive or negative charge) when dissolved in water. Typical examples include sodium, iron, calcium, magnesium, manganese, nitrate, chloride, sulfate, and zinc. Many of these chemicals are naturally occurring minerals that are dissolved from the rock/soil which make up the aquifer or water-bearing rock formations below the soil surface.

However, some of these compounds may be introduced into ground water by human activities. Nitrate (an agricultural fertilizer) and sodium chloride (road salt) are two examples. Water purveyors need to test for 30 different inorganic compounds including all arsenic, barium, cadmium, lead, mercury, selenium, and thallium

- ✓ **Organic compounds** - these are once living, or are living and can bring life to cells. These contain carbon, and their electrons spin clockwise, just like those of the human body. Additionally, these cells can form an ionic bond with the body and can easily break down into materials to help with bodily function, such as tissue repair.
- ✓ **Inorganic compounds**- these were never living, without carbon and cannot bring life to cells. The body treats these metals like toxins and are tightly held together; they cannot be easily broken down. And, their electrons spin counterclockwise, out of sync with the rest of the body.

Drinking Water Standards

The US Environmental Protection Agency is responsible for establishing maximum contaminant levels for drinking water. These standards are expressed as MCL (Maximum Contaminant Level). In most cases, this measurement is expressed as milligrams per liter of water (mg/l) or as parts per million (ppm).

In general terms, inorganic compounds are those materials that do not contain carbon. These compounds are often able to be dissolved in water. For example, dissolved gases such as nitrogen, oxygen, radon, and methane can be classified as inorganic compounds.

In addition to dissolved gases, some metals may be present in water as well. Some of these metals can be hazardous to human health, and may be introduced into water either naturally or through man-made activities.

Some of the more common metals include arsenic and aluminum which the EPA has established a MCL of no more than .05. Lead with a MCL of .015. Mercury MCL of .002. In addition, zinc, calcium, sodium, magnesium, potassium, and copper, all with a 1.3 MCL.

Lead, mercury, and arsenic can be dangerous to human health even at low concentrations, and as mentioned above can be introduced to our water from a variety of sources, including old pipes and lead solder. Conversely, some of the other inorganic compounds such as sodium, potassium, calcium, and magnesium are important to our overall health and well-being.

Another class of inorganic compounds are known as negative ions. These include substances such as fluoride: MCL 4.0 PPM (parts per million). Chloride and nitrate: MCL 10.0 ppm. Nitrite MCL 1.0. Sulfate, phosphate, carbonate, and cyanide: MCL 0.2

Inorganic Chemistry

Inorganic chemistry is the study of the synthesis and behavior of inorganic and organometallic compounds. This field covers all chemical compounds except the myriad organic compounds (carbon based compounds, usually containing C-H bonds), which are the subjects of organic chemistry. The distinction between the two disciplines is far from absolute, and there is much overlap, most importantly in the sub-discipline of organometallic chemistry. It has applications in every aspect of the chemical industry—including catalysis, materials science, pigments, surfactants, coatings, medicine, fuel, and agriculture.

Key Concepts

Many inorganic compounds are ionic compounds, consisting of cations and anions joined by ionic bonding. Examples of salts (which are ionic compounds) are magnesium chloride MgCl_2 , which consists of magnesium cations Mg^{2+} and chloride anions Cl^- ; or sodium oxide Na_2O , which consists of sodium cations Na^+ and oxide anions O^{2-} . In any salt, the proportions of the ions are such that the electric charges cancel out, so that the bulk compound is electrically neutral. The ions are described by their oxidation state and their ease of formation can be inferred from the ionization potential (for cations) or from the electron affinity (anions) of the parent elements.

Important classes of inorganic salts are the oxides, the carbonates, the sulfates and the halides. Many inorganic compounds are characterized by high melting points. Inorganic salts typically are poor conductors in the solid state. Another important feature is their solubility in water, e.g., and ease of crystallization. Where some salts (e.g., NaCl) are very soluble in water, others (e.g., SiO_2) are not.

The simplest inorganic reaction is double displacement when in mixing of two salts the ions are swapped without a change in oxidation state. In redox reactions one reactant, the *oxidant*, lowers its oxidation state and another reactant, the *reductant*, has its oxidation state increased. The net result is an exchange of electrons. Electron exchange can occur indirectly as well, e.g., in batteries, a key concept in electrochemistry.

When one reactant contains hydrogen atoms, a reaction can take place by exchanging protons in acid-base chemistry. In a more general definition, an acid can be any chemical species capable of binding to electron pairs is called a Lewis acid; conversely any molecule that tends to donate an electron pair is referred to as a Lewis base. As a refinement of acid-base interactions, the HSAB theory takes into account polarizability and size of ions.

Inorganic compounds are found in nature as minerals. Soil may contain iron sulfide as pyrite or calcium sulfate as gypsum. Inorganic compounds are also found multitasking as biomolecules: as electrolytes (sodium chloride), in energy storage (ATP) or in construction (the polyphosphate backbone in DNA).

The first important man-made inorganic compound was ammonium nitrate for soil fertilization through the Haber process. Inorganic compounds are synthesized for use as catalysts such as vanadium(V) oxide and titanium(III) chloride, or as reagents in organic chemistry such as lithium aluminum hydride.

Subdivisions of inorganic chemistry are organometallic chemistry, cluster chemistry and bioinorganic chemistry. These fields are active areas of research in inorganic chemistry, aimed toward new catalysts, superconductors, and therapies.

Industrial Inorganic Chemistry

Inorganic chemistry is a highly practical area of science. Traditionally, the scale of a nation's economy could be evaluated by their productivity of sulfuric acid. The top 20 inorganic chemicals manufactured in Canada, China, Europe, India, Japan, and the US (2005 data): aluminum sulfate, ammonia, ammonium nitrate, ammonium sulfate, carbon black, chlorine, hydrochloric acid, hydrogen, hydrogen peroxide, nitric acid, nitrogen, oxygen, phosphoric acid, sodium carbonate, sodium chlorate, sodium hydroxide, sodium silicate, sodium sulfate, sulfuric acid, and titanium dioxide. The manufacturing of fertilizers is another practical application of industrial inorganic chemistry.

Descriptive Inorganic Chemistry

Descriptive inorganic chemistry focuses on the classification of compounds based on their properties. Partly the classification focuses on the position in the periodic table of the heaviest element (the element with the highest atomic weight) in the compound, partly by grouping compounds by their structural similarities. When studying inorganic compounds, one often encounters parts of the different classes of inorganic chemistry (an organometallic compound is characterized by its coordination chemistry, and may show interesting solid state properties).

Different classifications are:

Coordination Compounds

Classical coordination compounds feature metals bound to "lone pairs" of electrons residing on the main group atoms of ligands such as H_2O , NH_3 , Cl^- , and CN^- . In modern coordination compounds almost all organic and inorganic compounds can be used as ligands. The "metal" usually is a metal from the groups 3-13, as well as the *trans*-lanthanides and *trans*-actinides, but from a certain perspective, all chemical compounds can be described as coordination complexes.

The stereochemistry of coordination complexes can be quite rich, as hinted at by Werner's separation of two enantiomers of $[\text{Co}((\text{OH})_2\text{Co}(\text{NH}_3)_4)_3]^{6+}$, an early demonstration that chirality is not inherent to organic compounds. A topical theme within this specialization is supramolecular coordination chemistry.

- **Examples:** $[\text{Co}(\text{EDTA})]^-$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $\text{TiCl}_4(\text{THF})_2$.

Main Group Compounds

These species feature elements from groups 1, 2 and 13-18 (excluding hydrogen) of the periodic table. Due to their often similar reactivity, the elements in group 3 (Sc, Y, and La) and group 12 (Zn, Cd, and Hg) are also generally included.

Main group compounds have been known since the beginnings of chemistry, e.g., elemental sulfur and the distillable white phosphorus. Experiments on oxygen, O_2 , by Lavoisier and Priestley not only identified an important diatomic gas, but opened the way for describing compounds and reactions according to stoichiometric ratios. The discovery of a practical synthesis of ammonia using iron catalysts by Carl Bosch and Fritz Haber in the early 1900s deeply impacted mankind, demonstrating the significance of inorganic chemical synthesis.

Typical main group compounds are SiO_2 , SnCl_4 , and N_2O . Many main group compounds can also be classed as "organometallic", as they contain organic groups, e.g., $\text{B}(\text{CH}_3)_3$. Main group compounds also occur in nature, e.g., phosphate in DNA, and therefore may be classed as bioinorganic. Conversely, organic compounds lacking (many) hydrogen ligands can be classed as "inorganic", such as the fullerenes, buckytubes and binary carbon oxides.

- **Examples:** tetrasulfur tetranitride S_4N_4 , diborane B_2H_6 , silicones, buckminsterfullerene C_{60} .

Transition Metal Compounds

Compounds containing metals from group 4 to 11 are considered transition metal compounds. Compounds with a metal from group 3 or 12 are sometimes also incorporated into this group, but also often classified as main group compounds.

Transition metal compounds show a rich coordination chemistry, varying from tetrahedral for titanium (e.g., TiCl_4) to square planar for some nickel complexes to octahedral for coordination complexes of cobalt. A range of transition metals can be found in biologically important compounds, such as iron in hemoglobin.

- **Examples:** iron pentacarbonyl, titanium tetrachloride, cisplatin

Organometallic Compounds

Usually, organometallic compounds are considered to contain the M-C-H group. The metal (M) in these species can either be a main group element or a transition metal. Operationally, the definition of an organometallic compound is more relaxed to include also highly lipophilic complexes such as metal carbonyls and even metal alkoxides.

Organometallic compounds are mainly considered a special category because organic ligands are often sensitive to hydrolysis or oxidation, necessitating that organometallic chemistry employs more specialized preparative methods than was traditional in Werner-type complexes.

Synthetic methodology, especially the ability to manipulate complexes in solvents of low coordinating power, enabled the exploration of very weakly coordinating ligands such as hydrocarbons, H_2 , and N_2 . Because the ligands are petrochemicals in some sense, the area of organometallic chemistry has greatly benefited from its relevance to industry.

- **Examples:** Cyclopentadienyliron dicarbonyl dimer $(C_5H_5)Fe(CO)_2CH_3$, Ferrocene $Fe(C_5H_5)_2$, Molybdenum hexacarbonyl $Mo(CO)_6$, Diborane B_2H_6 , Tetrakis(triphenylphosphine)palladium(0) $Pd[P(C_6H_5)_3]_4$

Cluster Compounds

Clusters can be found in all classes of chemical compounds. According to the commonly accepted definition, a cluster consists minimally of a triangular set of atoms that are directly bonded to each other. But metal-metal bonded dimetallic complexes are highly relevant to the area. Clusters occur in "pure" inorganic systems, organometallic chemistry, main group chemistry, and bioinorganic chemistry. The distinction between very large clusters and bulk solids is increasingly blurred. This interface is the chemical basis of nanoscience or nanotechnology and specifically arise from the study of quantum size effects in cadmium selenide clusters. Thus, large clusters can be described as an array of bound atoms intermediate in character between a molecule and a solid.

- **Examples:** $Fe_3(CO)_{12}$, $B_{10}H_{14}$, $[Mo_6Cl_{14}]^{2-}$, 4Fe-4S

Bioinorganic Compounds

By definition, these compounds occur in nature, but the subfield includes anthropogenic species, such as pollutants (e.g., methylmercury) and drugs (e.g., Cisplatin). The field, which incorporates many aspects of biochemistry, includes many kinds of compounds, e.g., the phosphates in DNA, and also metal complexes containing ligands that range from biological macromolecules, commonly peptides, to ill-defined species such as humic acid, and to water (e.g., coordinated to gadolinium complexes employed for MRI). Traditionally bioinorganic chemistry focuses on electron- and energy-transfer in proteins relevant to respiration. Medicinal inorganic chemistry includes the study of both non-essential and essential elements with applications to diagnosis and therapies.

- **Examples:** hemoglobin, methylmercury, carboxypeptidase

Solid State Compounds

This important area focuses on structure, bonding, and the physical properties of materials. In practice, solid state inorganic chemistry uses techniques such as crystallography to gain an understanding of the properties that result from collective interactions between the subunits of the solid. Included in solid state chemistry are metals and their alloys or intermetallic derivatives. Related fields are condensed matter physics, mineralogy, and materials science.

- **Examples:** silicon chips, zeolites, $\text{YBa}_2\text{Cu}_3\text{O}_7$

Theoretical Inorganic Chemistry

An alternative perspective on the area of inorganic chemistry begins with the Bohr model of the atom and, using the tools and models of theoretical chemistry and computational chemistry, expands into bonding in simple and then more complex molecules. Precise quantum mechanical descriptions for multielectron species, the province of inorganic chemistry, is difficult. This challenge has spawned many semi-quantitative or semi-empirical approaches including molecular orbital theory and ligand field theory. In parallel with these theoretical descriptions, approximate methodologies are employed, including density functional theory.

Exceptions to theories, qualitative and quantitative, are extremely important in the development of the field. For example, $\text{Cu}^{\text{II}}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ is almost diamagnetic below room temperature whereas Crystal Field Theory predicts that the molecule would have two unpaired electrons. The disagreement between qualitative theory (paramagnetic) and observation (diamagnetic) led to the development of models for "magnetic coupling." These improved models led to the development of new magnetic materials and new technologies.

Qualitative Theories

Inorganic chemistry has greatly benefited from qualitative theories. Such theories are easier to learn as they require little background in quantum theory. Within main group compounds, VSEPR theory powerfully predicts, or at least rationalizes, the structures of main group compounds, such as an explanation for why NH_3 is pyramidal whereas ClF_3 is T-shaped. For the transition metals, crystal field theory allows one to understand the magnetism of many simple complexes, such as why $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ has only one unpaired electron, whereas $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$ has five. A particularly powerful qualitative approach to assessing the structure and reactivity begins with classifying molecules according to electron counting, focusing on the numbers of valence electrons, usually at the central atom in a molecule.

Molecular Symmetry Group Theory

A central construct in inorganic chemistry is the theory of molecular symmetry. Mathematical group theory provides the language to describe the shapes of molecules according to their point group symmetry. Group theory also enables factoring and simplification of theoretical calculations.

Spectroscopic features are analyzed and described with respect to the symmetry properties of the, *inter alia*, vibrational or electronic states. Knowledge of the symmetry properties of the ground and excited states allows one to predict the numbers and intensities of absorptions in vibrational and electronic spectra. A classic application of group theory is the prediction of the number of C-O vibrations in substituted metal carbonyl complexes. The most common applications of symmetry to spectroscopy involve vibrational and electronic spectra. As an instructional tool, group theory highlights commonalities and differences in the bonding of otherwise disparate species, such as WF_6 and $\text{Mo}(\text{CO})_6$ or CO_2 and NO_2 .

Thermodynamics and Inorganic Chemistry

An alternative quantitative approach to inorganic chemistry focuses on energies of reactions. This approach is highly traditional and empirical, but it is also useful. Broad concepts that are couched in thermodynamic terms include redox potential, acidity, phase changes. A classic concept in inorganic thermodynamics is the Born-Haber cycle, which is used for assessing the energies of elementary processes such as electron affinity, some of which cannot be observed directly.

Mechanistic Inorganic Chemistry

An important and increasingly popular aspect of inorganic chemistry focuses on reaction pathways. The mechanisms of reactions are discussed differently for different classes of compounds.

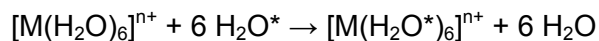
Main Group Elements and Lanthanides

The mechanisms of main group compounds of groups 13-18 are usually discussed in the context of organic chemistry (organic compounds are main group compounds, after all). Elements heavier than C, N, O, and F often form compounds with more electrons than predicted by the octet rule, as explained in the article on hypervalent molecules. The mechanisms of their reactions differ from organic compounds for this reason. Elements lighter than carbon (B, Be, Li) as well as Al and Mg often form electron-deficient structures that are electronically akin to carbocations. Such electron-deficient species tend to react via associative pathways. The chemistry of the lanthanides mirrors many aspects of chemistry seen for aluminum.

Transition Metal Complexes

Mechanisms for the reactions of transition metals are discussed differently from main group compounds. The important role of d-orbitals in bonding strongly influences the pathways and rates of ligand substitution and dissociation. These themes are covered in articles on coordination chemistry and ligand. Both associative and dissociative pathways are observed.

An overarching aspect of mechanistic transition metal chemistry is the kinetic lability of the complex illustrated by the exchange of free and bound water in the prototypical complexes $[\text{M}(\text{H}_2\text{O})_6]^{n+}$:

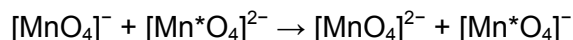


where H_2O^* denotes isotopically enriched water, e.g., $H_2^{17}O$

The rates of water exchange varies by 20 orders of magnitude across the periodic table, with lanthanide complexes at one extreme and Ir(III) species being the slowest.

Redox Reactions

Redox reactions are prevalent for the transition elements. Two classes of redox reaction are considered: atom-transfer reactions, such as oxidative addition/reductive elimination, and electron-transfer. A fundamental redox reaction is "self-exchange", which involves the degenerate reaction between an oxidant and a reductant. For example, permanganate and its one-electron reduced relative manganate exchange one electron:



Reactions at Ligands

Coordinated ligands display reactivity distinct from the free ligands. For example, the acidity of the ammonia ligands in $[Co(NH_3)_6]^{3+}$ is elevated relative to NH_3 itself. Alkenes bound to metal cations are reactive toward nucleophiles whereas alkenes normally are not. The large and industrially important area of catalysis hinges on the ability of metals to modify the reactivity of organic ligands. Homogeneous catalysis occurs in solution and heterogeneous catalysis occurs when gaseous or dissolved substrates interact with surfaces of solids. Traditionally homogeneous catalysis is considered part of organometallic chemistry and heterogeneous catalysis is discussed in the context of surface science, a subfield of solid state chemistry. But the basic inorganic chemical principles are the same. Transition metals, almost uniquely, react with small molecules such as CO , H_2 , O_2 , and C_2H_4 . The industrial significance of these feedstocks drives the active area of catalysis. Ligands can also undergo ligand transfer reactions such as transmetalation.

Characterization of Inorganic Compounds

Because of the diverse range of elements and the correspondingly diverse properties of the resulting derivatives, inorganic chemistry is closely associated with many methods of analysis. Older methods tended to examine bulk properties such as the electrical conductivity of solutions, melting points, solubility, and acidity. With the advent of quantum theory and the corresponding expansion of electronic apparatus, new tools have been introduced to probe the electronic properties of inorganic molecules and solids. Often these measurements provide insights relevant to theoretical models.

For example, measurements on the photoelectron spectrum of methane demonstrated that describing the bonding by the two-center, two-electron bonds predicted between the carbon and hydrogen using Valence Bond Theory is not appropriate for describing ionization processes in a simple way. Such insights led to the popularization of molecular orbital theory as fully delocalized orbitals are a more appropriate simple description of electron removal and electron excitation.

Commonly encountered techniques are:

- X-ray crystallography: This technique allows for the 3D determination of molecular structures.
- Dual polarization interferometer: This technique measures the conformation and conformational change of molecules.
- Various forms of spectroscopy
 - o Ultraviolet-visible spectroscopy: Historically, this has been an important tool, since many inorganic compounds are strongly colored
 - o NMR spectroscopy: Besides ^1H and ^{13}C many other "good" NMR nuclei (e.g., ^{11}B , ^{19}F , ^{31}P , and ^{195}Pt) give important information on compound properties and structure. Also the NMR of paramagnetic species can result in important structural information. Proton NMR is also important because the light hydrogen nucleus is not easily detected by X-ray crystallography.
 - o Infrared spectroscopy: Mostly for absorptions from carbonyl ligands
 - o Electron nuclear double resonance (ENDOR) spectroscopy
 - o Mössbauer spectroscopy
 - o Electron-spin resonance: ESR (or EPR) allows for the measurement of the environment of paramagnetic metal centers.
- Electrochemistry: Cyclic voltammetry and related techniques probe the redox characteristics of compounds.

Synthetic Inorganic Chemistry

Although some inorganic species can be obtained in pure form from nature, most are synthesized in chemical plants and in the laboratory.

Inorganic synthetic methods can be classified roughly according to the volatility or solubility of the component reactants. Soluble inorganic compounds are prepared using methods of organic synthesis. For metal-containing compounds that are reactive toward air, Schlenk line and glove box techniques are followed. Volatile compounds and gases are manipulated in "vacuum manifolds" consisting of glass piping interconnected through valves, the entirety of which can be evacuated to 0.001 mm Hg or less. Compounds are condensed using liquid nitrogen (b.p. 78K) or other cryogenics. Solids are typically prepared using tube furnaces, the reactants and products being sealed in containers, often made of fused silica (amorphous SiO_2) but sometimes more specialized materials such as welded Ta tubes or Pt "boats". Products and reactants are transported between temperature zones to drive reactions.

Drinking Water Analysis Chart

<u>ANALYSIS</u>	<u>METHOD</u>	<u>HOLDING TIME</u>
Inorganic Compounds (IOC) Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Copper, Iron, Lead, Manganese, Mercury, Nickel, Selenium, Silver, Sodium, Thallium, Zinc, Hardness, Conductivity, Turbidity, Color, Chloride, Cyanide, Fluoride, Nitrate, Nitrite, Sulfate, and Total Dissolved Solids.	(various)	48 hours
Primary Pollutants (Short IOC) Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Lead, Mercury, Selenium, Silver, Sodium, Thallium, Turbidity, Fluoride, Cyanide, Nitrate, and Nitrite.	(various)	48 hours
Municipal Testing		
Lead and Copper	EPA 200.9 for Pb EPA 200.7 for Cu	14 days
Public or Individual Water Source Testing		
Nitrate	SM-4500 NO3 D	48 hours
Total Coliform & E. Coli	SM-9223 B	30 Hours
Metals Analysis on Drinking Water (per element)		
GFAA (As, Pb, Sb, Se, Tl)	EPA 200.9	6 months
ICP (Ag, Al, B, Ba, Be, Cd, Cr, Cu, Fe, Mn, Mo, Na, Ni, Zn)	EPA 200.7	6 months
CVAA (Hg)	EPA 245.1	6 months
Primary Pollutant Metals	GFAA/ICP/CVAA	6 months
<u>Drinking Water Analysis</u>		
PH	EPA 150.1	
Acidity	SM-2310 B (4b)	14 days
Alkalinity (Bicarbonate & Carbonate)	SM-2320 B (4a)	14 days
BOD	SM-5210 B	48 hours
Calcium	EPA 200.7	6 months
Chloride	SM-4500 Cl	8 days
Chlorine, total	SM-4500 Cl	5 hours
Color	SM-2120 B	8 hours
COD	EPA 410.4 (7.3)	28 days
Cyanide	EPA 335.2 (8.7)	28 days
Dissolved Oxygen	SM-4500 O C	8 hours
Fluoride	SM-4500 F C	28 days

Hardness	SM-2340 B	6 months
Magnesium	EPA 200.7	6 months
Nitrogen, ammonia	SM-4500 NH3 E	28 days
	SM-4500 NH3 H	
Nitrogen, nitrate	SM-4500 NO3 D	48 hours
Nitrogen, nitrite	SM-4500 NO2	48 hours
Nitrate + Nitrite	SM-4500 NO3 E	48 hours
Nitrogen, TKN	EPA 351.4	28 days
Odor	SM-2150	6 days
Phosphorous, ortho	EPA 200.7	48 hours
Phosphorous, total	SM-4500 P	28 days
Solids, settle able	SM-2540	7 days
Solids, suspended	SM-2540 D	7 days
<u>Drinking Water Analysis</u>		
Solids, total	SM-2540 B	7 days
Solids, volatile	SM-2540 E	7 days
Specific Conductance	SM-2510 B	28 days
Sulfate	SM-4500 SO-4 E	28 days
Sulfide	SM-4500 S-2 D	28 days
Sulfite	EPA 377.1	28 days
Silica	SM-4500 SI E	28 days
Total Organic Carbon	EPA 415.1	28 days
Turbidity	SM- 2130 B	48 hours

<u>ORGANICS</u>		
Semi-volatile Organics in Water (SOC)*	(various)	7 days
Volatile Organics in Water*	(various)	7 days
Trihalomethanes*	EPA 501.1	7 days
Gross Alpha & Beta (Radionuclides)*	(various)	7 days
BOD	SM-5210 B	48 hours
COD	EPA 410.4(7.3)	28 days
Oil and Grease	EPA 413.1(1.2)	28 days
Hardness W/digestion	SM-2340 B	6 months
Nitrogen, TKN	EPA 351.4	28 days
Nitrogen, ammonia	SM-4500 NH3 F	28 days
Nitrogen, Total Organic	SM-4500 NorgNH3	28 days
Nitrogen, nitrate	SM-4500 NO3 D	48 hours
Nitrogen, nitrite	SM-4500 NO2 B	48 hours
Phosphorous, ortho	SM-4500 P E	48 hours
Sulfate	SM-4500 SO4 E	28 days
Solids, dissolved	SM-2540	7 days
Solids, settle able	SM-2540 F	7 days
Solids, suspended	SM-2540 D	7 days
Solids, total	SM-2540 B	7 days
Solids, volatile	SM-2540 E	7 days
Total Organic Carbon	EPA 415.1	28 days
PH	EPA 150.1	
Metals (per element)		

ICP (Ag, Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Sb, V)	EPA 200.7	6 months
GFAA (As, Pb, Ba, Se, Tl)	EPA 200.9	6 months
CVAA (Hg)	EPA 245.1	6 months

Definitions:

Action level - the concentration of a contaminant which, if exceeded, triggers treatment or other requirements which a water system must follow.

Maximum Contaminant Level - the "Maximum Allowed" (MCL) is the highest level of a contaminant that is allowed in drinking water. MCLs are set as close to the MCLGs as feasible using the best available treatment technology.

Maximum Contaminant Level Goal - the "Goal" (MCLG) is the level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety.

Non-Detects (ND) - laboratory analysis indicates that the constituent is not present.

Parts per million (ppm) or Milligrams per liter (mg/L) - one part per million corresponds to one minute in two years or a single penny in \$10,000.

Parts per billion (ppb) or Micrograms per liter (ug/L) - one part per billion corresponds to one minute in 2,000 years, or a single penny in \$10,000,000.

Picocuries per liter (pCi/L) - picocuries per liter is a measure of the radioactivity in water.

SAMPLE CONTAINERS and PRESERVATION

Methods used by the laboratory usually specify what type of container and how much sample is required to run an analysis. The following table provides a summary of the sample handling and preservation requirements for some of the most common tests.

Parameter	Bottle Type	Minimum Sample Size	Maximum Holding Time	Storage & Preservation
Acidity	P or G ^B	100ml	24 hrs/14 days	refrigerate
Alkalinity	P or G	200ml	24 hrs/14 days	refrigerate
BOD (5 day)	P or G	1L	6 hrs/48 hrs	refrigerate
Boron	P	100ml	28 days/6 months	
Chloride	P or G	250ml	28 days	
Chlorine, residual	P or G	500ml	0.5 hr/stat	analyze on site ASAP
COD	P or G	500ml	28 days/28 days	analyze on site ASAP
Color	P or G	500ml	48 hrs/48 hrs	refrigerate
Coliform, Total	P or G	125ml	30 hrs	refrigerate
Conductivity	P or G	500ml	48 hrs/48 hrs	refrigerate
Cyanide, Total	P or G	500ml	28 days/28 days	add NaOH to pH>12
				refrigerate in dark
Fluoride	P	300ml	28days/ 28 days	
Hardness	P or G	100ml	6 months/6 months	add HNO ₃ to pH<2
Metals, general	P ^A or G ^A	250ml	6 months/6 months	add HNO ₃ to pH<2
<i>Furnace</i>	P ^A or G ^A	250ml	6 months/6 months	
<i>Flame</i>	P ^A or G ^A	250ml	6 months/6 months	
Mercury	P ^A or G ^A	500ml	28 days/28 days	add HNO ₃ to pH<2
Nitrogen	P or G	500ml	7 days/ 28 days	ASAP or add H ₂ SO ₄ to pH<2 & refrigerate
<i>Ammonia</i>				
<i>Nitrate</i>	P or G	100ml	48 hrs/48	ASAP &

			hrs	refrigerate
<i>Nitrate + Nitrite</i>	P or G	200ml	48 hrs/28 days	ASAP & refrigerate
<i>Nitrite</i>	P or G	100ml	none/48 hrs	ASAP & refrigerate
<i>TKN</i>	P or G	500ml	7 days/28 days	add H ₂ SO ₄ to pH<2
Oxygen, dissolved	G (BOD)	300ml		
<i>Electrode</i>			0.5 hrs/stat	ASAP on site
<i>Winkler</i>			8hrs/8 hrs	ASAP on site
pH	P or G	50ml	2 hrs/stat	ASAP on site
Phosphate,	G ^A			
<i>Ortho</i>		100ml	48hrs	filter ASAP refrigerate
<i>Total</i>		100ml	28 days/28 days	refrigerate
Solids,	P or G			
<i>Dissolved</i>		250ml	7 days	refrigerate
<i>Settleable</i>		1L	48 hrs	refrigerate
<i>Suspended</i>		250ml	7 days	refrigerate
<i>Total</i>		250ml	7 days	refrigerate
<i>Volatile</i>		250ml	7 days	refrigerate
Silica	P	200ml	28 days/28 days	refrigerate
Sulfate	P or G	100ml	28 days/28 days	refrigerate
Turbidity	P or G	100ml	24 hrs/48 hrs	ASAP/refrigerate, store in dark up to 24 hrs

Refrigerate = storage at 4 degrees C, in the dark. P = plastic (polyethylene or equivalent); G = glass, G^A or P^A = rinsed with 1:1 HNO₃; G^B = glass, borosilicate, G^S = glass rinsed with organic solvents; NS = not stated in cited reference; stat = no storage allowed; analyze immediately.

Chain of Custody Procedures

Because a sample is physical evidence, chain of custody procedures are used to maintain and document sample possession from the time the sample is collected until it is introduced as evidence. Chain of custody requirements will vary from agency to agency.

However, these procedures are similar and the chain of custody outlined in this manual is only a guideline. Consult your project manager for specific requirements.

If you have physical possession of a sample, have it in view, or have physically secured it to prevent tampering then it is defined as being in **“custody.”** A chain of custody record, therefore, begins when the sample containers are obtained from the laboratory. From this point on, a chain of custody record will accompany the sample containers.

Handle the samples as little as possible in the field. Each custody sample requires a chain of custody record and may require a seal. If you do not seal individual samples, then seal the containers in which the samples are shipped.

When the samples transfer possession, both parties involved in the transfer must sign, date and note the time on the chain of custody record. If a shipper refuses to sign the chain-of-custody you must seal the samples and chain of custody documents inside a box or cooler with bottle seals or evidence tape. The recipient will then attach the shipping invoices showing the transfer dates and times to the custody sheets. If the samples are split and sent to more than one laboratory, prepare a separate chain of custody record for each sample. If the samples are delivered to after-hours night drop-off boxes, the custody record should note such a transfer and be locked with the sealed samples inside sealed boxes.



Using alcohol to disinfect a special sample tap before obtaining a sample.

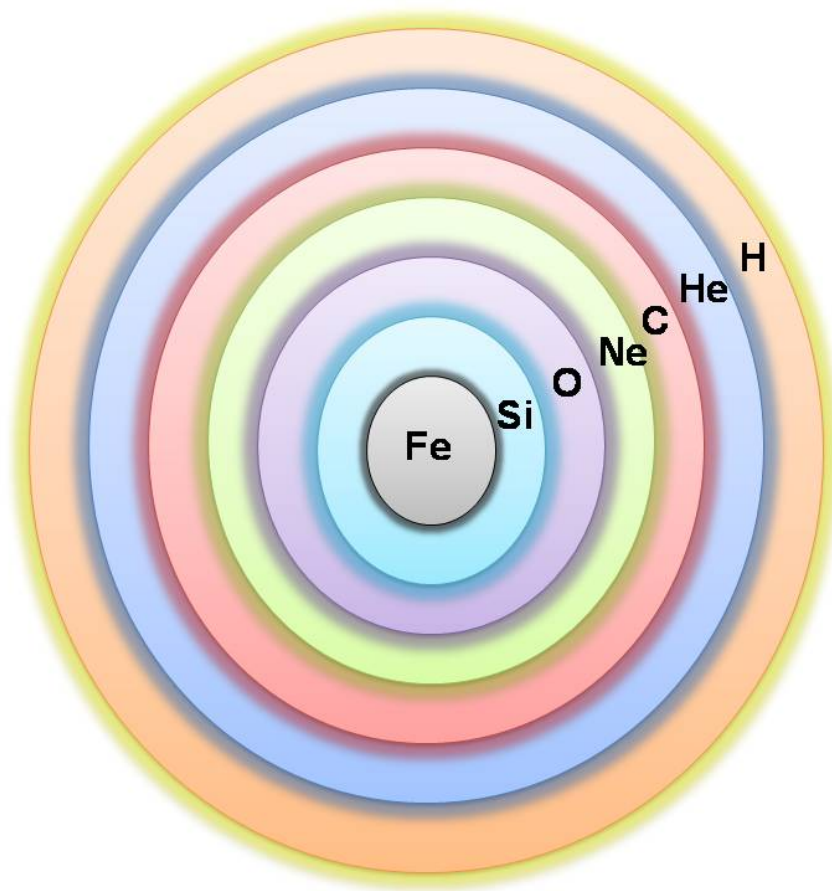
Laboratory 123 W. Main St Sun City, Arizona 85541										LAB I.D. NUMBER													
DATE: _____ PAGE 1 OF 1																							
Sampler: _____																							
Company: _____ Department: _____ Address: _____ Contact: _____ Telephone: _____																							
Sample Identification	Date	Time	Matrix	Lab ID	Metals* See Attached	TSS	Lead/Copper	BOD/COD	Nitrate	Nitrate + Nitrite	TKN / Ammonia	VOC / THM's	Semi Volatil Organics (625)	Chloride	Cyanide	Fluoride	Surfactants (MBAS)	Tot. Coliform MPN	Fecal Coliform MPN-HPC	Organo-Phosphorus Pest. (8141)	Sulfate	EC Conductivity	Number/Containers
Project Name					Sample Receipt					RELINQUISHED BY:					RELINQUISHED BY:								
					No. Containers: _____					Signature: _____					Signature: _____								
					Custody Seals: _____					Printed Name: _____					Printed Name: _____								
					Received Intact: _____					Company _____					Company _____								
Field Measurements:					Received Cold: _____					SAMPLED RECEIVED BY:					SAMPLED RECEIVED BY:								
pH: _____					Temperature: _____					Signature: _____					Signature: _____								
Temp: _____					PRIORITY: _____					Printed Name: _____					Printed Name: _____								
										Company _____					Company _____								

Chain of Custody Example.

Periodic Table of the Elements

The image consists of two side-by-side photographs of mineral specimens. The left photograph shows a large, irregularly shaped piece of a metallic mineral, likely pyrite, characterized by its brilliant golden-brown luster and visible crystalline structure. The right photograph shows a close-up of a large quantity of small, dark gray to black, angular mineral grains, possibly hematite or magnetite, piled together.

(866) 557-1746 Fax (928) 468-0675



Fe: Iron

Si: Silicon

O: Oxygen

Ne: Neon

C: Carbon

He: Helium

H: Hydrogen

Elements of a star

Metalloid Section

Drinking water contaminants that can cause health effects after continuous long-term exposure at levels greater than the maximum contaminant level (MCL) are considered “chronic” contaminants. Examples of chronic drinking water contaminants regulated by EPA include inorganic contaminants like arsenic, cadmium, and copper; organic contaminants such as pesticides and industrial chemicals; and radiological contaminants like radium and uranium.

If your water system has installed some form of inorganic contaminant or arsenic treatment, keep in mind that the treatment you installed may change the water quality in other ways. It might cause the water to react differently in the distribution system. Depending on the kind of treatment you’ve installed, consider what distribution system problems might result.

A change in the taste, odor or appearance of the water at customers’ taps may be the first indication of a problem. Some water quality parameters to consider monitoring, depending on your arsenic treatment technology, include iron, pH, manganese, alkalinity, and aluminum.

In contrast, “acute” contaminants can cause short-term health effects within hours or days of exposure. Microbes such as *E. coli* and *Cryptosporidium* are examples of contaminants that can cause an acute health risk. Some chronic-type contaminants can also fall in this category if they are present at high enough concentrations to cause immediate health effects. For example, nitrate levels over the MCL can cause “blue-baby” syndrome in children less than 6 months.

Arsenic, boron, silicon, germanium, antimony and tellurium are commonly classified as metalloids. One or more from among selenium, polonium or astatine are sometimes added to the list. Boron is sometimes excluded from the list, by itself or together with silicon. Tellurium is sometimes not regarded as a metalloid. The inclusion of antimony, polonium and astatine as metalloids has also been questioned

A metalloid is a chemical element with properties that are in-between or a mixture of those of metals and nonmetals, and which is considered to be difficult to classify unambiguously as either a metal or a nonmetal. There is no standard definition of a metalloid nor is there agreement as to which elements are appropriately classified as such. Despite this lack of specificity the term continues to be used in the chemistry literature.

Some authors do not classify elements bordering the metal-nonmetal dividing line as metalloids noting that a binary classification can facilitate the establishment of some simple rules for determining bond types between metals and/or nonmetals. Other authors, in contrast, have suggested that classifying some elements as metalloids 'emphasizes that properties change gradually rather than abruptly as one moves across or down the periodic table. Alternatively, some periodic tables distinguish elements that are metalloids in the absence of any formal dividing line between metals and nonmetals. Metalloids are instead shown as occurring in a diagonal fixed band or diffuse region, running from upper left to lower right, centered around arsenic.

The six elements commonly recognized as metalloids are boron, silicon, germanium, arsenic, antimony and tellurium. They are metallic-looking brittle solids, with intermediate to relatively good electrical conductivities, and each having the electronic band structure of either a semiconductor or a semimetal.

Chemically, they mostly behave as (weak) nonmetals, have intermediate ionization energy and electronegativity values, and form amphoteric or weakly acidic oxides. Being too brittle to have any structural uses, the metalloids and their compounds instead find common use in glasses, alloys and semiconductors. The electrical properties of silicon and germanium, in particular, enabled the establishment of the semiconductor industry in the 1950s and the development of solid state electronics from the early 60s onwards.

Other elements less commonly recognized as metalloids include carbon, aluminum, selenium, polonium and astatine. On a standard periodic table these elements, as well as the elements commonly recognized as metalloids, occur in or near a diagonal region of the p-block, having its main axis anchored by boron at one end and astatine at the other. Some periodic tables include a dividing line between metals and nonmetals and it is generally the elements adjacent to this line or, less frequently, one or more of the elements adjacent to those elements, which are identified as metalloids.

The term *metalloid* was first popularly used to refer to nonmetals. It's more recent meaning as a category of elements with intermediate or hybrid properties did not become widespread until the period 1940–1960. Metalloids are sometimes called semimetals, a practice which has been discouraged. This is because the term *semimetal* has a different meaning in physics, one which more specifically refers to the electronic band structure of a substance rather than the overall classification of a chemical element.

There is no universally agreed or rigorous definition of a metalloid. The feasibility of establishing a specific definition has also been questioned, noting anomalies can be found in several such attempted constructs. Classifying any particular element as a metalloid has been described as 'arbitrary'.

The generic definition set out at the start of this article is based on metalloid attributes consistently cited in the literature. Illustrative definitions and extracts include:

- 'In chemistry a metalloid is an element with properties intermediate between those of metals and nonmetals.'
- 'Between the metals and nonmetals in the periodic table we find elements...[that] share some of the characteristic properties of both the metals and nonmetals, making it difficult to place them in either of these two main categories.'
- 'Chemists sometimes use the name metalloid...for these elements which are difficult to classify one way or the other.'
- 'Because the traits distinguishing metals and nonmetals are qualitative in nature, some elements do not fall unambiguously in either category. These elements...are called metalloids...'

More Broadly, Metalloids have also been referred to as:

- 'elements that...are somewhat of a cross between metals and nonmetals' or
- 'weird in-between elements.'

The criterion that metalloids are difficult to unambiguously classify one way or the other is a key tenet. In contrast, elements such as sodium and potassium 'have metallic properties to a high degree' and fluorine, chlorine and oxygen 'are almost exclusively nonmetallic.'

Although most other elements have a mixture of metallic and nonmetallic properties most such elements can also be classified as either metals or nonmetals according to which set of properties are regarded as being more pronounced in them. It is only the elements at or near the margins, ordinarily those that are regarded as lacking a sufficiently clear preponderance of metallic or nonmetallic properties, which are classified as metalloids.

Which Elements are Metalloids?

There is no universally agreed or rigorous definition of the term metalloid. So the answer to the question "Which elements are metalloids?" can vary, depending on the author and their inclusion criteria. Emsley, for example, recognized only four: germanium, arsenic, antimony and tellurium. James et al., on the other hand, listed twelve: boron, carbon, silicon, germanium, arsenic, selenium, antimony, tellurium, bismuth, polonium, ununpentium and livermorium. As of 2011 the list of metalloid lists recorded an average of just over seven elements classified as metalloids, per list of metalloids, based on a sample size of 194 lists.

The absence of a standardized division of the elements into metals, metalloids and nonmetals is not necessarily an issue. There is a more or less continuous progression from the metallic to the nonmetallic. A specified subset of this continuum can potentially serve its particular purpose as well as any other. In any event, individual metalloid classification arrangements tend to share common ground (as described above) with most variations occurring around the indistinct margins, as surveyed later.

How Are Chronic Contaminants Regulated?

In 1974, Congress passed the Safe Drinking Water Act (SDWA) to give EPA the authority to set standards to ensure the safety of drinking water provided by public water systems. The SDWA, which was amended in 1986 and 1996, directs EPA to establish non-enforceable health goals called maximum contaminant level goals (MCLGs) which reflect the level at which no adverse health effects are expected from a particular contaminant.

Once an MCLG is established, EPA sets enforceable standards for contaminants called maximum contaminant levels (MCLs). MCLs are set as close to the health goals as possible considering cost, benefits, and the ability of public water systems to detect and remove contaminants using appropriate treatment technologies. When there is no reliable method to measure a contaminant that is economically and technically feasible, EPA develops a treatment technique requirement rather than an MCL. EPA continues to assess the occurrence of unregulated contaminants through the Unregulated Contaminant Monitoring Regulation (UCMR). Information about the UCMR can be found at <http://www.epa.gov/safewater/ucmr/>.

What Are Some Best Practices For Effective Communication About Chronic Contaminants?

If you expect that your public water system will exceed EPA's standard for a contaminant or that the costs of compliance may require public funding, communicate early and often. The most effective communication efforts follow these simple steps:

- Provide simple, straightforward, *and consistent* messages;
- Describe potential adverse health effects and populations at risk;
- Describe actions you are taking to correct the situation and when you anticipate it will be resolved;
- Describe actions the consumer can take such as using alternate water supplies and when to seek medical help;
- Provide links to useful information resources such as EPA's Web site.
- Use graphics, photographs, maps, charts, and drawings to illustrate your messages;
- Assume that consumers will only read the top half of the notice or what can be read in ten seconds;
- Display important elements in bold and/or large type in the top half of the notice;
- Communicate in multiple languages to meet the needs of your non-English speaking consumers; and Include contact information for further information in *all* communications.

Near Metalloids

The concept of a class of elements intermediate between metals and nonmetals is sometimes extended to include elements that most chemists, and related science professionals, would not ordinarily recognize as metalloids. In 1935, Fernellius and Robey allocated carbon, phosphorus, selenium, and iodine to such an intermediary class of elements, together with boron, silicon, arsenic, antimony, tellurium and polonium. They also included a placeholder for the missing element 85 (astatine), five years ahead of its synthesis in 1940.

They excluded germanium from their considerations as it was still then regarded as a poorly conducting metal. In 1954, Szabó & Lakatos counted beryllium and aluminum in their list of metalloids, as well as boron, silicon, germanium, arsenic, antimony, tellurium, polonium and astatine. In 1957, Sanderson recognized carbon, phosphorus, selenium, and iodine as part of an intermediary class of elements with 'certain metallic properties', together with boron, silicon, arsenic, tellurium, and astatine. Germanium, antimony and polonium were classified by him as metals. More recently, in 2007, Petty included carbon, phosphorus, selenium, tin and bismuth in his list of metalloids, as well as boron, silicon, germanium, arsenic, antimony, tellurium, polonium and astatine.

Elements such as these are occasionally called, or described as, *near-metalloids*, or the like. They are located near the elements commonly recognized as metalloids, and usually classified as either metals or nonmetals. Metals falling into this loose category tend to show 'odd' packing structures, marked covalent chemistry (molecular or polymeric), and amphoterism. Aluminum, tin and bismuth are examples. They are also referred to as (*chemically*) *weak metals*, *poor metals*, *post-transition metals*, or *semimetals* (in the aforementioned sense of metals with incomplete metallic character). These classification groupings generally cohabit the same periodic table territory but are not necessarily mutually inclusive.

Nonmetals in the 'near-metalloid' category include carbon, phosphorus, selenium and iodine. They exhibit metallic luster, semiconducting properties and bonding or valence bands with delocalized character. This applies to their most thermodynamically stable forms under ambient conditions: carbon as graphite; phosphorus as black phosphorus; and selenium as grey selenium. These elements are alternatively described as being 'near metalloid(al)', showing metalloid(al) character, or having metalloid-like or some metalloid(al) or metallic properties.

Allotropes

Some allotropes of the elements exhibit more pronounced metallic, metalloid(al) or nonmetallic behavior than others. For example, the diamond allotrope of carbon is clearly nonmetallic. The graphite allotrope however displays limited electrical conductivity more characteristic of a metalloid. Phosphorus, selenium, tin, and bismuth also have allotropes that display borderline or either metallic or nonmetallic behavior.

Categorization and Periodic Table Territory

Metalloids are generally regarded as a third category of chemical elements, alongside metals and nonmetals. They have been described as forming a (fuzzy) buffer zone between metals and nonmetals. The make-up and size of this zone depends on the classification criteria being used. Metalloids are sometimes grouped instead with metals, regarded as nonmetals or treated as a sub-category of same.

Metalloid Border

H								He	
Li	Be			B	C	N	O	F	Ne
Na	Mg			Al	Si	P	S	Cl	Ar
K	Ca	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Cn	Uut	Fl	Uup	Lv	Uus	Uuo	

Periodic table extract showing elements that have sometimes¹ been classified as metalloids:

Elements that appear commonly to rarely in the list of metalloid lists.

Elements that appear still less frequently.

Outlying elements showing that the metalloid net is sometimes cast very widely. Although they do not appear in the list of metalloids lists, isolated references to their designation as metalloids can be found in the literature.

Metalloids cluster on either side of the **dividing line between metals and nonmetals**. This can be found, in varying configurations, on some periodic tables (see mini-example, right). Elements to the lower left of the line generally display increasing metallic behavior; elements to the upper right display increasing nonmetallic behavior. When presented as a regular stair-step, elements with the highest critical temperature for their groups (Li, Be, Al, Ge, Sb, Po) lie just below the line.

The diagonal positioning of the metalloids represents somewhat of an exception to the phenomenon that elements with similar properties tend to occur in vertical columns. Going across a periodic table row, the nuclear charge increases with atomic number just as there is as a corresponding increase in electrons. The additional 'pull' on outer electrons with increasing nuclear charge generally outweighs the screening efficacy of having more electrons. With some irregularities, atoms therefore become smaller, ionization energy increases, and there is a gradual change in character, across a period, from strongly metallic, to weakly metallic, to weakly nonmetallic, to strongly nonmetallic elements.

Going down a main group periodic table column, the effect of increasing nuclear charge is generally outweighed by the effect of additional electrons being further away from the nucleus. With some irregularities, atoms therefore become larger, ionization energy falls, and metallic character increases. The combined effect of these competing horizontal and vertical trends is that the location of the metal-nonmetal transition zone shifts to the right in going down a period.

A related effect can be seen in other diagonal similarities that occur between some elements and their lower right neighbors, such as lithium-magnesium, beryllium-aluminum, carbon-phosphorus, and nitrogen-sulfur.

Other Metalloids

Given there is no agreed definition of a metalloid, some other elements are occasionally classified as such. These elements include hydrogen, beryllium, nitrogen, phosphorus, sulfur, zinc, gallium, tin, iodine, lead, bismuth and radon. The term metalloid has also been used to refer to:

- Elements that exhibit metallic luster and electrical conductivity, and that are also amphoteric. Arsenic, antimony, vanadium, chromium, molybdenum, tungsten, tin, lead and aluminum are examples.
- Elements that are otherwise sometimes referred to as poor metals.
- Nonmetallic elements (for example, nitrogen; carbon) that can form alloys with, or modify the properties of, metals.

Heavy Metals

A heavy metal is a member of a loosely defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. The term *heavy metal* has been called a "misinterpretation" in an IUPAC technical report due to the contradictory definitions and its lack of a "coherent scientific basis". There is an alternative term *toxic metal*, for which no consensus of exact definition exists either. As discussed below, depending on context, heavy metal can include elements lighter than carbon and can exclude some of the heaviest metals. Heavy metals occur naturally in the ecosystem with large variations in concentration. In modern times, anthropogenic sources of heavy metals, i.e. pollution, have been introduced to the ecosystem. Waste-derived fuels are especially prone to contain heavy metals, so heavy metals are a concern in consideration of waste as fuel.

Motivations for controlling heavy metal concentrations in gas streams are diverse. Some of them are dangerous to health or to the environment (e.g. mercury, cadmium, lead, chromium), some may cause corrosion (e.g. zinc, lead), some are harmful in other ways (e.g. arsenic may pollute catalysts). Within the European community the eleven elements of highest concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, and thallium, the emissions of which are regulated in waste incinerators. Some of these elements are actually necessary for humans in minute amounts (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead, arsenic), the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium).

Heavy metal pollution can arise from many sources but most commonly arises from the purification of metals, e.g., the smelting of copper and the preparation of nuclear fuels. Electroplating is the primary source of chromium and cadmium. Through precipitation of their compounds or by ion exchange into soils and muds, heavy metal pollutants can localize and lay dormant. Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation. Currently, plants or microorganisms are tentatively used to remove some heavy metals such as mercury.

Plants which exhibit hyper accumulation can be used to remove heavy metals from soils by concentrating them in their bio matter. Some treatment of mining tailings has occurred where the vegetation is then incinerated to recover the heavy metals.

One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and biomagnification causing heavier exposure for some organisms than is present in the environment alone. Coastal fish (such as the smooth toadfish) and seabirds (such as the Atlantic Puffin) are often monitored for the presence of such contaminants.

Living organisms require varying amounts of "heavy metals". Iron, cobalt, copper, manganese, molybdenum, and zinc are required by humans. Excessive levels can be damaging to the organism. Other heavy metals such as mercury, plutonium, and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can cause serious illness. Certain elements that are normally toxic are, for certain organisms or under certain conditions, beneficial. Examples include vanadium, tungsten, and even cadmium.

Toxic Metals

Toxic metals are metals that form poisonous soluble compounds and have no biological role, i.e. are not essential minerals, or are in the wrong form. Often heavy metals are thought as synonymous, but lighter metals also have toxicity, such as beryllium, and not all heavy metals are particularly toxic, and some are essential, such as iron. The definition may also include trace elements when considered in abnormally high, toxic doses. A difference is that there is no beneficial dose for a toxic metal with no biological role.

Toxic metals sometimes imitate the action of an essential element in the body, interfering with the metabolic process to cause illness. Many metals, particularly heavy metals are toxic, but some heavy metals are essential, and some, such as bismuth, have a low toxicity. Most often the definition includes at least cadmium, lead, mercury and the radioactive metals. Metalloids (arsenic, polonium) may be included in the definition.

Radioactive metals have both radiological toxicity and chemical toxicity. Metals in an oxidation state abnormal to the body may also become toxic: chromium (III) is an essential trace element, but chromium (VI) is a carcinogen.

Toxicity is a function of solubility. Insoluble compounds as well as the metallic forms often exhibit negligible toxicity. The toxicity of any metal depends on its ligands. In some cases, organometallic forms, such as dimethyl mercury and tetraethyl lead, can be extremely toxic. In other cases, organometallic derivatives are less toxic such as the cobaltocenium cation.

Decontamination for toxic metals is different from organic toxins: because toxic metals are elements, they cannot be destroyed. Toxic metals may be made insoluble or collected, possibly by the aid of chelating agents. Toxic metals can bioaccumulate in the body and in the food chain. Therefore, a common characteristic of toxic metals is the chronic nature of their toxicity. This is particularly notable with radioactive heavy metals such as thorium, which imitates calcium to the point of being incorporated into human bone, although similar health implications are found in lead or mercury poisoning. The exceptions to this are barium and aluminum, which can be removed efficiently by the kidneys.

Toxic Heavy Metals

- Antimony (a metalloid)
- Arsenic is a metalloid
- Barium
- Beryllium
- Cadmium - cadmium poisoning
- Lead - lead poisoning
- Mercury - mercury poisoning
- Osmium
- Thallium
- Vanadium
- Radioactive metals:
 - o Actinium
 - o Thorium
 - o Uranium
 - o Radium
 - o The transuraniums, such as plutonium, americium, etc.
 - o Polonium
 - o Radioactive isotopes of metallic elements not otherwise strongly toxic, e.g. cobalt-60 and strontium-90.

Aluminum has no biological role and its classification into toxic metals is controversial. Significant toxic effects and accumulation to tissues have been observed in renally impaired patients. However, individuals with healthy kidneys can be exposed to large amounts of aluminum with no ill effects. Thus, aluminum is not considered dangerous to persons with normal elimination capacity.

Trace Elements with Toxicity

- Chromium as hexavalent Cr(VI)
- Nickel – nickel salts are carcinogenic
- Copper – copper toxicity
- Zinc - zinc toxicity
- Iron – iron poisoning
- Fluorine-fluoride poisoning

Nonmetals

Some heavy nonmetals may be erroneously called "metals", because they have some metallic properties.

- Selenium – a nonmetal; essential element
- Tellurium

Atomic Spectrometry

Atomic spectrometry converts each metal in the water sample to a particulate emission that can then be weighed. Extrapolations are made to determine each metal concentration in each water sample taken. The complicated analysis requires preserving the sample with acid, heating the sample to convert to a particulate emission and then identifying each metal and its weight.

A simple analogy is to capture the steam from a pot of water, separate every atom in the steam, identify each atom, weigh each atom and then apply these numbers back to the original volume of water contained in the pot. The result is an accurate picture of what is in the water.

Heavy Metals in Water

High heavy metals concentrations can be naturally occurring. Every geologic formation contains a certain amount of heavy metal. Mine operations extract and process these metals in areas with the highest concentrations. Water in these areas may have high metal concentrations due to the combination of naturally occurring deposits and mine waste. Water samples are usually taken randomly within a contaminated area and offsite to identify the source of contamination and the pathway it travels, into the drinkable groundwater system or away from potable water sources. Accurate determination of heavy metal contamination is important to identify cumulative risks to people drinking water derived from these areas.

Treating Heavy Metal Contamination in Water

Heavy metal water contamination is a difficult expensive problem to address. Most cleanup activities use a pump and treat system where contaminated groundwater is pumped out of the ground, treated with activated carbon to remove contaminants and then replaced into the groundwater system. Because large volumes of water must be pumped and treated over long time periods, associated operation and maintenance systems are very expensive. There are some new technologies being developed that actually treat the water in the ground which operate more efficiently and quickly, decreasing costs.

If groundwater is contaminated with heavy metals, an alternative source of drinking water must be used to prevent harmful health effects, until the water is treated to meet standards protective of human health and the environment

Health Significance of Metals in the Environment

The metallic elements can be categorized into two groups. The heavy metals are those having densities five times greater than water, and the light metals, those having lesser densities. Well-known examples of heavy metallic elements are iron, lead, and copper. Examples of light metals are sodium, magnesium, and potassium. Humans consume metallic elements through both water and food. Some metals such as sodium, potassium, magnesium, calcium, and iron are found in living tissue and are essential to human life—biological anomalies arise when they are depleted or removed. Probably less well known is that currently no less than six other heavy metals including molybdenum, manganese, cobalt, copper, and zinc, have been linked to human growth, development, achievement, and reproduction (Vahrenkamp, 1979; Friberg and others, 1979). Even these metals, however, can become toxic or aesthetically undesirable when their concentrations are too great. Several heavy metals, like cadmium, lead, and mercury, are highly toxic at relatively low concentrations, can accumulate in body tissues over long periods of time, and are nonessential for human health. Table 1 lists metals according to their toxicities.

No specific health guidelines for heavy metals associated with suspended or bed sediments have been established by the U.S. Environmental Protection Agency. This lack of national guidelines based on concise scientific criteria causes difficulty when evaluating the environmental effects of heavy metals in sediments. Several different criteria have been defined, primarily on the basis of observed effects on aquatic life (Lyman and others, 1987). Table 2 lists criteria for open-water disposal of polluted sediments that can be used for comparison purposes.

Table 1. Classification of naturally occurring metals according to their toxicity and availability in the hydrologic environment (from Wood, 1974)

[Metals that normally do not exist as dissolved species in natural waters or are very rare in crustal rocks are in italics]

Nontoxic		Low toxicity			Moderate to high toxicity		
Aluminum	Magnesium	Barium	<i>Praseodymium</i>	<i>Actinium</i>	Indium	Polonium	Uranium
Bismuth	Manganese	<i>Cerium</i>	<i>Promethium</i>	Antimony	<i>Iridium</i>	<i>Radium</i>	Vanadium
Calcium	Molybdenum	<i>Dysprosium</i>	<i>Rhenium</i>	Beryllium	Lead	<i>Ruthenium</i>	Zinc
Cesium	Potassium	<i>Erbium</i>	<i>Rhodium</i>	Boron	Mercury	Silver	<i>Zirconium</i>
Iron	Strontium	<i>Europium</i>	<i>Samarium</i>	Cadmium	Nickel	<i>Tantalum</i>	
Lithium	Rubidium	<i>Gadolinium</i>	Scandium	Chromium	<i>Niobium</i>	Thallium	
	Sodium	<i>Gallium</i>	<i>Terbium</i>	Cobalt	<i>Osmium</i>	Thorium	
		Germanium	Thulium	Copper	Palladium	<i>Titanium</i>	
		<i>Gold</i>	<i>Tin</i>	<i>Hafnium</i>	Platinum	<i>Tungsten</i>	
		<i>Holmium</i>	<i>Ytterbium</i>				
		<i>Neodymium</i>	Yttrium				

Table 2. U.S. Environmental Protection Agency maximum contaminant levels for heavy-metal concentrations in drinking water and water supporting aquatic life, and criteria for open-water disposal of polluted sediments

[$\mu\text{g/L}$, microgram per liter; $\mu\text{g/g}$, microgram per gram; >, greater than; <, less than; --, no guideline available]

	Cadmium	Chromium	Copper	Lead	Mercury	Uranium
Drinking water, in $\mu\text{g/L}$ ¹	5	100	² 1,000	15	2	³ 20
Water supporting aquatic life, in $\mu\text{g/L}$ ⁴	12	100	20	100	0.05	—
Natural sediments, nonpolluted, in $\mu\text{g/g}$ ⁵	--	<25	<25	<40	<1	—
Natural sediments, moderately polluted, in $\mu\text{g/g}$ ⁵	--	25 to 75	25 to 50	40 to 60	--	—
Natural sediments, heavily polluted, in $\mu\text{g/g}$ ⁵	>6	>75	>50	>60	>1	—

¹U.S. Environmental Protection Agency, 1992.

²Secondary maximum contaminant level based on esthetic water quality.

³Proposed maximum contaminant level.

⁴U.S. Environmental Protection Agency, 1982.

⁵Great Lakes Water Quality Board, Dredging Subcommittee, 1982.

Antimony - Inorganic Contaminant 0.006 mg/L MCL Metalloid

Antimony is a toxic chemical element with symbol **Sb** and atomic number 51. A lustrous gray metalloid, it is found in nature mainly as the sulfide mineral stibnite (Sb_2S_3). Antimony compounds have been known since ancient times and were used for cosmetics; metallic antimony was also known, but it was erroneously identified as lead. It was established to be an element around the 17th century.

For some time, China has been the largest producer of antimony and its compounds, with most production coming from the Xikuangshan Mine in Hunan. The industrial methods to produce antimony are roasting and subsequent carbothermal reduction or direct reduction of stibnite with iron.

What are EPA's drinking water regulations for antimony?

In 1974, Congress passed the Safe Drinking Water Act. This law requires EPA to determine the level of contaminants in drinking water at which no adverse health effects are likely to occur. These non-enforceable health goals, based solely on possible health risks and exposure over a lifetime with an adequate margin of safety, are called maximum contaminant level goals (MCLG). Contaminants are any physical, chemical, biological or radiological substances or matter in water.



The MCLG for antimony is 0.006 mg/L or 6 ppb. EPA has set this level of protection based on the best available science to prevent potential health problems. EPA has set an enforceable regulation for antimony, called a maximum contaminant level (MCL), at 0.006 mg/L or 6 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies. In this case, the MCL equals the MCLG, because analytical methods or treatment technology do not pose any limitation.

The Phase V Rule, the regulation for antimony, became effective in 1994. The Safe Drinking Water Act requires EPA to periodically review the national primary drinking water regulation for each contaminant and revise the regulation, if appropriate. EPA reviewed antimony as part of the Six Year Review and determined that the 0.006 mg/L or 6 ppb MCLG and 0.006 mg/L or 6 ppb MCL for antimony are still protective of human health.

Applications

The largest applications for metallic antimony are as alloying material for lead and tin and for lead antimony plates in lead-acid batteries. Alloying lead and tin with antimony improves the properties of the alloys which are used in solders, bullets and plain bearings. Antimony compounds are prominent additives for chlorine- and bromine-containing fire retardants found in many commercial and domestic products. An emerging application is the use of antimony in microelectronics.

Antimony is in the nitrogen group (group 15) and has an electronegativity of 2.05. As expected by periodic trends, it is more electronegative than tin or bismuth, and less electronegative than tellurium or arsenic. Antimony is stable in air at room temperature, but reacts with oxygen if heated to form antimony trioxide, Sb_2O_3 . Antimony is a silvery, lustrous gray metal that has a Mohs scale hardness of 3. Therefore, pure antimony is not used to make hard objects: coins made of antimony were issued in China's Guizhou province in 1931, but because of their rapid wear, their minting was discontinued. Antimony is resistant to attack by acids.

Four allotropes of antimony are known, a stable metallic form and three metastable forms, explosive, black and yellow. Metallic antimony is a brittle, silver-white shiny metal. When molten antimony is slowly cooled, metallic antimony crystallizes in a trigonal cell, isomorphic with that of the gray allotrope of arsenic. A rare explosive form of antimony can be formed from the electrolysis of antimony (III) trichloride. When scratched with a sharp implement, an exothermic reaction occurs and white fumes are given off as metallic antimony is formed; when rubbed with a pestle in a mortar, a strong detonation occurs.

Black antimony is formed upon rapid cooling of vapor derived from metallic antimony. It has the same crystal structure as red phosphorus and black arsenic; it oxidizes in air and may ignite spontaneously. At 100 °C, it gradually transforms into the stable form. The yellow allotrope of antimony is the most unstable. It has only been generated by oxidation of stibine (SbH_3) at -90 °C. Above this temperature and in ambient light, this metastable allotrope transforms into the more stable black allotrope.

Metallic antimony adopts a layered structure (space group $R\bar{3}m$ No. 166) in which layers consist of fused ruffled six-membered rings. The nearest and next-nearest neighbors form a distorted octahedral complex, with the three atoms in the same double-layer being slightly closer than the three atoms in the next. This relatively close packing leads to a high density of 6.697 g/cm³, but the weak bonding between the layers leads to the low hardness and brittleness of antimony.

Isotopes

Antimony exists as two stable isotopes, ^{121}Sb with a natural abundance of 57.36% and ^{123}Sb with a natural abundance of 42.64%. It also has 35 radioisotopes, of which the longest-lived is ^{125}Sb with a half-life of 2.75 years. In addition, 29 metastable states have been characterized. The most stable of these is ^{124}Sb with a half-life of 60.20 days, which has an application in some neutron sources. Isotopes that are lighter than the stable ^{123}Sb tend to decay by β^+ decay, and those that are heavier tend to decay by β^- decay, with some exceptions.

Occurrence

The abundance of antimony in the Earth's crust is estimated at 0.2 to 0.5 parts per million, comparable to thallium at 0.5 parts per million and silver at 0.07 ppm. Even though this element is not abundant, it is found in over 100 mineral species. Antimony is sometimes found natively, but more frequently it is found in the sulfide stibnite (Sb_2S_3) which is the predominant ore mineral.

Antimony compounds are often classified into those of Sb(III) and Sb(V). Relative to its congener arsenic, the +5 oxidation state is more stable.

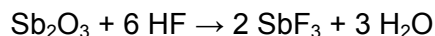
Oxides and hydroxides

Antimony trioxide (Sb_2O_3) is formed when antimony is burnt in air. In the gas phase, this compound exists as Sb_4O_6 , but it polymerizes upon condensing. Antimony pentoxide (Sb_2O_5) can only be formed by oxidation by concentrated nitric acid. Antimony also forms a mixed-valence oxide, antimony tetroxide (Sb_2O_4), which features both Sb(III) and Sb(V). Unlike phosphorus and arsenic, these various oxides are amphoteric, do not form well-defined oxoacids and react with acids to form antimony salts.

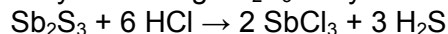
Antimonous acid $\text{Sb}(\text{OH})_3$ is unknown, but the conjugate base sodium antimonite ($[\text{Na}_3\text{SbO}_3]_4$) forms upon fusing sodium oxide and Sb_2O_3 . Transition metal antimonites are also known. Antimonic acid exists only as the hydrate $\text{HSb}(\text{OH})_6$, forming salts containing the antimonate anion $\text{Sb}(\text{OH})_6^-$. Dehydrating metal salts containing this anion yields mixed oxides. Many antimony ores are sulfides, including stibnite (Sb_2S_3), pyargyrite (Ag_3SbS_3), zinkenite, jamesonite, and boulangerite. Antimony pentasulfide is non-stoichiometric and features antimony in the +3 oxidation state and S-S bonds. Several thioantimonides are known, such as $[\text{Sb}_6\text{S}_{10}]^{2-}$ and $[\text{Sb}_8\text{S}_{13}]^{2-}$.

Halides

Antimony forms two series of halides, SbX_3 and SbX_5 . The trihalides SbF_3 , SbCl_3 , SbBr_3 , and SbI_3 are all molecular compounds having trigonal pyramidal molecular geometry. The trifluoride SbF_3 is prepared by the reaction of Sb_2O_3 with HF:



It is Lewis acidic and readily accepts fluoride ions to form the complex anions SbF_4^- and SbF_6^- . Molten SbF_3 is a weak electrical conductor. The trichloride SbCl_3 is prepared by dissolving Sb_2S_3 in hydrochloric acid:

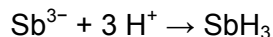


The pentahalides SbF_5 and SbCl_5 have trigonal bipyramidal molecular geometry in the gas phase, but in the liquid phase, SbF_5 is polymeric, whereas SbCl_5 is monomeric. SbF_5 is a powerful Lewis acid used to make the super acid fluoroantimonic acid (" HSbF_6 ").

Oxyhalides are more common for antimony than arsenic and phosphorus. Antimony trioxide dissolves in concentrated acid to form oxoantimonyl compounds such as SbOCl and $(\text{SbO})_2\text{SO}_4$.

Antimonides, hydrides, and organoantimony compounds

Compounds in this class generally are described as derivatives of Sb^{3-} . Antimony forms antimonides with metals, such as indium antimonide (InSb) and silver antimonide (Ag_3Sb). The alkali metal and zinc antimonides, such as Na_3Sb and Zn_3Sb_2 , are more reactive. Treating these antimonides with acid produces the unstable gas stibine, SbH_3 :



Stibine can also be produced by treating Sb^{3+} salts with hydride reagents such as sodium borohydride. Stibine decomposes spontaneously at room temperature. Because stibine has a positive heat of formation, it is thermodynamically unstable and thus antimony does not react with hydrogen directly.

Organoantimony compounds are typically prepared by alkylation of antimony halides with Grignard reagents. A large variety of compounds are known with both Sb(III) and Sb(V) centers, including mixed chloro-organic derivatives, anions, and cations. Examples include $\text{Sb}(\text{C}_6\text{H}_5)_3$ (triphenylstibine), $\text{Sb}_2(\text{C}_6\text{H}_5)_4$ (with an Sb-Sb bond), and cyclic $[\text{Sb}(\text{C}_6\text{H}_5)]_n$. Pentacoordinated organoantimony compounds are common, examples being $\text{Sb}(\text{C}_6\text{H}_5)_5$ and several related halides.

History

Antimony(III) sulfide, Sb_2S_3 , was recognized in predynastic Egypt as an eye cosmetic (kohl) as early as about 3100 BC, when the cosmetic palette was invented.

An artifact, said to be part of a vase, made of antimony dating to about 3000 BC was found at Telloh, Chaldea (part of present-day Iraq), and a copper object plated with antimony dating between 2500 BC and 2200 BC has been found in Egypt. Austen, at a lecture by Herbert Gladstone in 1892 commented that "we only know of antimony at the present day as a highly brittle and crystalline metal, which could hardly be fashioned into a useful vase, and therefore this remarkable 'find' (artifact mentioned above) must represent the lost art of rendering antimony malleable."

Moorey was unconvinced the artifact was indeed a vase, mentioning that Selimkhanov, after his analysis of the Tello object (published in 1975), "attempted to relate the metal to Transcaucasian natural antimony" (i.e. native metal) and that "the antimony objects from Transcaucasia are all small personal ornaments." This weakens the evidence for a lost art "of rendering antimony malleable."

The first European description of a procedure for isolating antimony is in the book *De la pirotechnia* of 1540 by Vannoccio Biringuccio; this predates the more famous 1556 book by Agricola, *De re metallica*. In this context Agricola has been often incorrectly credited with the discovery of metallic antimony. The book *Currus Triumphalis Antimonii* (The Triumphal Chariot of Antimony), describing the preparation of metallic antimony, was published in Germany in 1604. It was purported to have been written by a Benedictine monk, writing under the name Basilius Valentinus, in the 15th century; if it were authentic, which it is not, it would predate Biringuccio.

The first natural occurrence of pure antimony in the Earth's crust was described by the Swedish scientist and local mine district engineer Anton von Swab in 1783; the type-sample was collected from the Sala Silver Mine in the Bergslagen mining district of Sala, Västmanland, Sweden.

Astatine- Nonmetal or a Metalloid

Astatine may be a nonmetal or a metalloid. It is ordinarily classified as a nonmetal, but has some 'marked' metallic properties. Immediately following its production in 1940, early investigators considered it to be a metal. In 1949 it was called the most noble (difficult to reduce) nonmetal as well as being a relatively noble (difficult to oxidize) metal. In 1950 astatine was described as a halogen and (therefore) a reactive nonmetal.

In terms of metallic indicators:

- Samsonov observes that, '[L]ike typical metals, it is precipitated by hydrogen sulfide even from strongly acid solutions and is displaced in a free form from sulfate solutions; it is deposited on the cathode on electrolysis'.
- Rossler cites further indications of a tendency for astatine to behave like a (heavy) metal as: '...the formation of pseudohalide compounds...complexes of astatine cations...complex anions of trivalent astatine...as well as complexes with a variety of organic solvents'.
- Rao and Ganguly note that elements with an enthalpy of vaporization (EoV) greater than ~42 kJ/mol are metallic when liquid. Such elements include boron, silicon, germanium, antimony, selenium and tellurium. Vásáros & Berei give estimated values for the EoV of diatomic astatine, the lowest of these being 50 kJ/mol. On this basis astatine may also be metallic in the liquid state. Diatomic iodine, with an EoV of 41.71, falls just short of the threshold figure.
- Siekierski and Burgess contend or presume that astatine would be a metal if it could form a condensed phase.
- Champion et al. argue that astatine demonstrates cationic behavior, by way of stable At^+ and AtO^+ forms, in strongly acidic aqueous solutions.



For Nonmetallic Indicators:

- Batsanov gives a calculated band gap energy for astatine of 0.7 eV. This is consistent with nonmetals (in physics) having separated valence and conduction bands and thereby being either semiconductors or insulators.
- It has the narrow liquid range ordinarily associated with nonmetals (mp 575 K, bp 610).
- Its chemistry in aqueous solution is predominately characterized by the formation of various anionic species.
- Most of its known compounds resemble those of iodine, which is halogen and a nonmetal. Such compounds include astatides (XAt), astatates (XAtO_3), and monovalent interhalogen compounds.

Restrepo et al. reported that astatine appeared to share more in common with polonium than it did with the established halogens. They did so on the basis of detailed comparative studies of the known and interpolated properties of 72 elements.

Other Metalloids

Given there is no agreed definition of a metalloid, some other elements are occasionally classified as such. These elements include hydrogen, beryllium, nitrogen, phosphorus, sulfur, zinc, gallium, tin, iodine, lead, bismuth and radon. The term metalloid has also been used to refer to:

- Elements that exhibit metallic luster and electrical conductivity, and that are also amphoteric. Arsenic, antimony, vanadium, chromium, molybdenum, tungsten, tin, lead and aluminum are examples.
- Elements that are otherwise sometimes referred to as poor metals.
- Nonmetallic elements (for example, nitrogen; carbon) that can form alloys with, or modify the properties of, metals.
- Nonmetals in the 'near-metallloid' category include carbon, phosphorus, selenium and iodine. They exhibit metallic luster, semiconducting properties and bonding or valence bands with delocalized character. This applies to their most thermodynamically stable forms under ambient conditions: carbon as graphite; phosphorus as black phosphorus; and selenium as grey selenium. These elements are alternatively described as being 'near metalloid', showing metalloid character, or having metalloid-like or some metalloid(al) or metallic properties.

Boron - Metalloid

Boron is a chemical element with chemical symbol **B** and atomic number 5. Because boron is produced entirely by cosmic ray spallation and not by stellar nucleosynthesis, it is a low-abundance element in both the solar system and the Earth's crust. Boron is concentrated on Earth by the water-solubility of its more common naturally occurring compounds, the borate minerals. These are mined industrially as evaporites, such as borax and kernite.

Chemically uncombined boron, which is classed as a metalloid, is not found naturally on Earth. Industrially, very pure boron is produced with difficulty, as boron tends to form refractory materials containing small amounts of carbon or other elements. Several allotropes of boron exist: amorphous boron is a brown powder and crystalline boron is black, extremely hard (about 9.5 on the Mohs scale), and a poor conductor at room temperature. Elemental boron is used as a dopant in the semiconductor industry.



The major industrial-scale uses of boron compounds are in sodium perborate bleaches, and the borax component of fiberglass insulation. Boron polymers and ceramics play specialized roles as high-strength lightweight structural and refractory materials. Boron compounds are used in silica-based glasses and ceramics to give them resistance to thermal shock. Boron-containing reagents are used for as intermediates in the synthesis of organic fine chemicals. A few boron-containing organic pharmaceuticals are used, or are in study. Natural boron is composed of two stable isotopes, one of which (boron-10) has a number of uses as a neutron-capturing agent.

In biology, borates have low toxicity in mammals (similar to table salt), but are more toxic to arthropods and are used as insecticides. Boric acid is mildly antimicrobial, and a natural boron-containing organic antibiotic is known. Boron is essential to life. Small amounts of boron compounds play a strengthening role in the cell walls of all plants, making boron necessary in soils. Experiments indicate a role for boron as an ultratrace element in animals, but the nature of its role in animal physiology is unknown.

Boron compounds were known thousands of years ago. Borax was known from the deserts of western Tibet, where it received the name of *tincal*, derived from the Sanskrit. Borax glazes were used in China from AD300, and some tincal even reached the West, where the Persian alchemist Jābir ibn Hayyān seems to mention it in 700. Marco Polo brought some glazes back to Italy in the 13th century. Agricola, around 1600, reports the use of borax as a flux in metallurgy. In 1777, boric acid was recognized in the hot springs (soffioni) near Florence, Italy, and became known as *sal sedativum*, with mainly medical uses.

The rare mineral is called sassolite, which is found at Sasso, Italy. Sasso was the main source of European borax from 1827 to 1872, at which date American sources replaced it. Boron compounds were relatively rarely used chemicals until the late 1800s when Francis Marion Smith's Pacific Coast Borax Company first popularized these compounds and made them in volume and hence cheap.

Boron was not recognized as an element until it was isolated by Sir Humphrey Davy and by Joseph Louis Gay-Lussac and Louis Jacques Thénard. In 1808 Davy observed that electric current sent through a solution of borates produced a brown precipitate on one of the electrodes. In his subsequent experiments he used potassium to reduce boric acid instead of electrolysis. He produced enough boron to confirm a new element and named the element *boracium*.

Gay-Lussac and Thénard used iron to reduce boric acid at high temperatures. They showed by oxidizing boron with air that boric acid is an oxidation product of boron. Jöns Jakob Berzelius identified boron as an element in 1824. Pure boron was arguably first produced by the American chemist Ezekiel Weintraub in 1909.

Chemical Compounds

In its most familiar compounds, boron has the formal oxidation state III. These include oxides, sulfides, nitrides, and halides. The trihalides adopt a planar trigonal structure. These compounds are Lewis acids in that they readily form adducts with electron-pair donors, which are called Lewis bases. For example, fluoride (F^-) and boron trifluoride (BF_3) combined to give the tetrafluoroborate anion, BF_4^- . Boron trifluoride is used in the petrochemical industry as a catalyst. The halides react with water to form boric acid.

Boron is found in nature on Earth entirely as various oxides of B (III), often associated with other elements. The more than one hundred borates all feature boron in oxidation state +3. These minerals resemble silicates in some respect, although boron is often found not only in a tetrahedral coordination with oxygen, but also in a trigonal planar configuration. Unlike silicates, the boron minerals never feature boron with coordination number greater than four. A typical motif is exemplified by the tetraborate anions of the common mineral borax. The formal negative charge of the tetrahedral borate centers is balanced by metal cations in the minerals, such as the sodium (Na^+) in borax.

Boron Nitride

The boron nitrides are notable for the variety of structures that they adopt. They adopt structures analogous to various allotropes of carbon, including graphite, diamond, and nanotubes. In the diamond-like structure called cubic boron nitride (tradename Borazon), boron atoms exist in the tetrahedral structure of carbons atoms in diamond, but one in every four B-N bonds can be viewed as a coordinate covalent bond, wherein two electrons are donated by the nitrogen atom which acts as the Lewis base to a bond to the Lewis acidic boron (III) center.

Cubic boron nitride, among other applications, is used as an abrasive, as it has a hardness comparable with diamond (the two substances are able to produce scratches on each other). In the BN compound analogue of graphite, hexagonal boron nitride (h-BN), the positively-charged boron and negatively-charged nitrogen atoms in each plane lie adjacent to the oppositely charged atom in the next plane. Consequently graphite and h-BN have very different properties, although both are lubricants, as these planes slip past each other easily. However, h-BN is a relatively poor electrical and thermal conductor in the planar directions.

Organoboron Chemistry

A large number of organoboron compounds are known and many are useful in organic synthesis. Organoboron (III) compounds are usually tetrahedral or trigonal planar, for example, tetraphenylborate ($\text{B}(\text{C}_6\text{H}_5)_4^-$) vs triphenylborane ($\text{B}(\text{C}_6\text{H}_5)_3$). Many are produced from hydroboration, which employs diborane (B_2H_6).

Compounds of B(I) and B(II)

Although these are not found on Earth naturally, boron forms a variety of stable compounds with formal oxidation state less than three. As for many covalent compounds, formal oxidation states are often of little meaning in boron hydrides and metal borides. The halides also form derivatives of B(I) and B(II). BF , isoelectronic with N_2 , is not isolable in condensed form, but B_2F_4 and B_4Cl_4 are well characterized.

Binary metal-boron compounds, the metal borides, feature boron in oxidation state less than III. Illustrative is magnesium diboride (MgB_2). Each boron atom has a formal -1 charge and magnesium is assigned a formal charge of $2+$. In this material, the boron centers are trigonal planar, with an extra double bond for each boron, with the boron atoms forming sheets akin to the carbon in graphite. However, unlike the case with hexagonal boron nitride which by comparison lacks electrons in the plane of the covalent atoms, the delocalized electrons in the plane of magnesium diboride allow it to conduct electricity similar to isoelectronic graphite. In addition, in 2001 this material was found to be a high-temperature superconductor. Certain other metal borides find specialized applications as hard materials for cutting tools.

From the structural perspective, the most distinctive chemical compounds of boron are the hydrides. Included in this series are the cluster compounds dodecaborate ($\text{B}_{12}\text{H}_{12}^{2-}$), decaborane ($\text{B}_{10}\text{H}_{14}$), and the carboranes such as $\text{C}_2\text{B}_{10}\text{H}_{12}$. Characteristically such compounds feature boron with coordination numbers greater than four.

Isotopes

Boron has two naturally occurring and stable isotopes, ^{11}B (80.1%) and ^{10}B (19.9%). The mass difference results in a wide range of $\delta^{11}\text{B}$ values, which are defined as a fractional difference between the ^{11}B and ^{10}B and traditionally expressed in parts per thousand, in natural waters ranging from -16 to $+59$. There are 13 known isotopes of boron, the shortest-lived isotope is ^7B which decays through proton emission and alpha decay. It has a half-life of 3.5×10^{-22} s. Isotopic fractionation of boron is controlled by the exchange reactions of the boron species $\text{B}(\text{OH})_3$ and $[\text{B}(\text{OH})_4]^-$. Boron isotopes are also fractionated during mineral crystallization, during H_2O phase changes in hydrothermal systems, and during hydrothermal alteration of rock. The latter effect results in preferential removal of the $^{10}\text{B}(\text{OH})_4$ ion onto clays. It results in solutions enriched in $^{11}\text{B}(\text{OH})_3$ and therefore may be responsible for the large ^{11}B enrichment in seawater relative to both oceanic crust and continental crust; this difference may act as an isotopic signature. The exotic ^{17}B exhibits a nuclear halo, i.e. its radius is appreciably larger than that predicted by the liquid drop model.

The ^{10}B isotope is good at capturing thermal neutrons. Natural boron is about 20% ^{10}B and 80% ^{11}B . The nuclear industry enriches natural boron to nearly pure ^{10}B . The less-valuable by-product, depleted boron, is nearly pure ^{11}B .

Commercial Isotope Enrichment

Because of its high neutron cross-section, boron-10 is often used to control fission in nuclear reactors as a neutron-capturing substance. Several industrial-scale enrichment processes have been developed, however only the fractionated vacuum distillation of the dimethyl ether adduct of boron trifluoride (DME-BF₃) and column chromatography of borates are being used.

Enriched Boron (boron-10)

Is used in neutron capture therapy of cancer. In the latter ("boron neutron capture therapy" or BNCT), a compound containing ¹⁰B is incorporated into a pharmaceutical which is selectively taken up by a malignant tumor and tissues near it. The patient is then treated with a beam of either thermal neutrons, or else neutrons of low energy, at a relatively low neutron radiation dose. The neutrons, however, trigger energetic and short-range secondary alpha particle and lithium-7 heavy ion radiation that are products of the boron + neutron nuclear reaction, and this ion radiation additionally bombards the tumor, especially from inside the tumor cells.

In nuclear reactors, ¹⁰B is used for reactivity control and in emergency shutdown systems. It can serve either function in the form of borosilicate control rods or as boric acid. In pressurized water reactors, boric acid is added to the reactor coolant when the plant is shut down for refueling. It is then slowly filtered out over many months as fissile material is used up and the fuel becomes less reactive.

In future manned interplanetary spacecraft, ¹⁰B has a theoretical role as structural material (as boron fibers or BN nanotube material) which would also serve a special role in the radiation shield. One of the difficulties in dealing with cosmic rays, which are mostly high energy protons, is that some secondary radiation from interaction of cosmic rays and spacecraft materials is high energy spallation neutrons. Such neutrons can be moderated by materials high in light elements such as polyethylene, but the moderated neutrons continue to be a radiation hazard unless actively absorbed in the shielding. Among light elements that absorb thermal neutrons, ⁶Li and ¹⁰B appear as potential spacecraft structural materials which serve both for mechanical reinforcement and radiation protection.

Depleted Boron (boron-11)

Cosmic radiation will produce secondary neutrons if it hits spacecraft structures. Those neutrons will be captured in ¹⁰B, if it is present in the spacecraft's semiconductors, producing a gamma ray, an alpha particle, and a lithium ion. These resultant decay products may then irradiate nearby semiconductor 'chip' structures, causing data loss (bit flipping, or single event upset). In radiation hardened semiconductor designs, one countermeasure is to use **depleted boron** which is greatly enriched in ¹¹B and contains almost no ¹⁰B. ¹¹B is largely immune to radiation damage. Depleted boron is a by-product of the nuclear industry.

¹¹B is also a candidate as a fuel for aneutronic fusion. When struck by a proton with energy of about 500 keV, it produces three alpha particles and 8.7 MeV of energy. Most other fusion reactions involving hydrogen and helium produce penetrating neutron radiation, which weakens reactor structures and induces long term radioactivity thereby endangering operating personnel. Whereas, the alpha particles from ¹¹B fusion can be turned directly into electric power, and all radiation stops as soon as the reactor is turned off.

Applications

Nearly all boron ore extracted from the Earth is destined for refinement into boric acid and sodium tetraborate pentahydrate. In the United States, 70% of the boron is used for the production of glass and ceramics.

Glass and Ceramics

Borosilicate glass, which is typically 12–15% B_2O_3 , 80% SiO_2 , and 2% Al_2O_3 , has a low coefficient of thermal expansion giving it a good resistance to thermal shock. Duran and Pyrex are two major brand names for this glass, used both in laboratory glassware and in consumer cookware and bakeware, chiefly for this resistance.

Boron filaments are high-strength, lightweight materials that are used chiefly for advanced aerospace structures as a component of composite materials, as well as limited production consumer and sporting goods such as golf clubs and fishing rods. The fibers can be produced by chemical vapor deposition of boron on a tungsten filament.

Boron fibers and sub-millimeter sized crystalline boron springs are produced by laser-assisted chemical vapor deposition. Translation of the focused laser beam allows producing even complex helical structures. Such structures show good mechanical properties (elastic modulus 450 GPa, fracture strain 3.7%, fracture stress 17 GPa) and can be applied as reinforcement of ceramics or in micromechanical systems.

Detergent Formulations and Bleaching Agents

Borax is used in various household laundry and cleaning products, including the well-known "20 Mule Team Borax" laundry booster and "Boraxo" powdered hand soap. It is also present in some tooth bleaching formulas.

Sodium perborate serves as a source of active oxygen in many detergents, laundry detergents, cleaning products, and laundry bleaches. However, despite its name, "Borateem" laundry bleach no longer contains any boron compounds, using sodium percarbonate instead as a bleaching agent.

Insecticides

Boric acid is used as an insecticide, notably against ants, fleas, and cockroaches.

Semiconductors

Boron is a useful dopant for such semiconductors as silicon, germanium, and silicon carbide. Having one fewer valence electron than the host atom, it donates a hole resulting in p-type conductivity. Traditional method of introducing boron into semiconductors is via its atomic diffusion at high temperatures. This process uses either solid (B_2O_3), liquid (BBr_3), or gaseous boron sources (B_2H_6 or BF_3). However, after 1970s, it was mostly replaced by ion implantation, which relies mostly on BF_3 as a boron source. Boron trichloride gas is also an important chemical in semiconductor industry, however not for doping but rather for plasma etching of metals and their oxides. Triethylborane is also injected into vapor deposition reactors as a boron source. Examples are the plasma deposition of boron-containing hard carbon films, silicon nitride-boron nitride films, and for doping of diamond film with boron.

Magnets

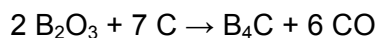
Boron is a component of neodymium magnets ($\text{Nd}_2\text{Fe}_{14}\text{B}$), which are the strongest type of permanent magnet. They are found in a variety of domestic and professional electromechanical and electronic devices, such as magnetic resonance imaging (MRI), various motors and actuators, computer HDDs, CD and DVD players, mobile phones, timer switches, speakers, and so on.

High-Hardness and Abrasive Compounds

Several boron compounds are known for their extreme hardness and toughness. Boron carbide and cubic boron nitride powders are widely used as abrasives. Metal borides are used for coating tools through chemical vapor deposition or physical vapor deposition. Implantation of boron ions into metals and alloys, through ion implantation or ion beam deposition, results in a spectacular increase in surface resistance and microhardness. Laser alloying has also been successfully used for the same purpose. These borides are an alternative to diamond coated tools, and their (treated) surfaces have similar properties to those of the bulk boride.

Boron Carbide

Boron carbide is a ceramic material which is obtained by decomposing B_2O_3 with carbon in the electric furnace:



Boron carbide's structure is only approximately B_4C , and it shows a clear depletion of carbon from this suggested stoichiometric ratio. This is due to its very complex structure. The substance can be seen with empirical formula B_{12}C_3 (i.e., with B_{12} dodecahedra being a motif), but with less carbon as the suggested C_3 units are replaced with B-C chains, and there are smaller (B_6) octahedra present as well. (See the article for structural analysis).

The repeating polymer plus semi-crystalline structure of boron carbide gives it great structural strength per weight. It is used in tank armor, bulletproof vests, and numerous other structural applications.

Boron carbide's ability to absorb neutrons without forming long-lived radionuclides (especially when doped with extra boron-10) makes the material attractive as an absorbent for neutron radiation arising in nuclear power plants. Nuclear applications of boron carbide include shielding, control rods and shut-down pellets. Within control rods, boron carbide is often powdered, to increase its surface area.

Other Super Hard Boron Compounds

- Heterodiamond (also called BCN);
- Boron nitride. This material is isoelectronic to carbon. Similar to carbon, it has both hexagonal (soft graphite-like h-BN) and cubic (hard, diamond-like c-BN) forms. h-BN is used as a high temperature component and lubricant. c-BN, also known under commercial name borazon, is a superior abrasive. Its hardness is only slightly smaller, but chemical stability is superior to that of diamond.
- Rhenium diboride can be produced at ambient pressures, but is rather expensive because of rhenium. The hardness of ReB_2 exhibits considerable anisotropy because of its hexagonal layered structure. Its value is comparable to that of tungsten carbide, silicon carbide, titanium diboride or zirconium diboride.

Germanium- Metalloid

Germanium looks like a metal. It has a bright, shiny, silvery color. But it is brittle and breaks apart rather easily, which metals normally do not do. It has a melting point of 937.4°C (1,719°F) and a boiling point of 2,830°C (5,130°F). It conducts an electric current poorly. Substances of this kind are called semiconductors. Semiconductors conduct an electric current, but not nearly as well as metals like silver, copper, and aluminum.

The ability of semiconductors to conduct electricity depends greatly on the presence of small amounts of impurities. The addition of an impurity to a semiconductor is called doping. Doping a semiconductor has significant effects on its ability to conduct an electric current.

Germanium is a chemical element with symbol Ge and atomic number 32. It is a lustrous, hard, grayish-white metalloid in the carbon group, chemically similar to its group neighbor's tin and silicon.

Purified germanium is a semiconductor, with an appearance most similar to elemental silicon. Like silicon, germanium naturally reacts and forms complexes with oxygen in nature. Unlike silicon, it is too reactive to be found naturally on Earth in the free (native) state.



Because very few minerals contain it in high concentration, germanium was discovered comparatively late in the history of chemistry. Germanium ranks near fiftieth in relative abundance of the elements in the Earth's crust. In 1869, Dmitri Mendeleev predicted its existence and some of its properties based on its position on his periodic table and called the element ekasilicon. Nearly two decades later, in 1886, Clemens Winkler found the new element along with silver and sulfur, in a rare mineral called argyrodite. Although the new element somewhat resembled arsenic and antimony in appearance, its combining ratios in the new element's compounds agreed with Mendeleev's predictions for a predicted relative of silicon. Winkler named the element after his country, Germany. Today, germanium is mined primarily from sphalerite (the primary ore of zinc), though germanium is also recovered commercially from silver, lead, and copper ores.

Germanium "metal" (isolated germanium) is used as semiconductor in transistors and various other electronic devices. Historically the first decade of semiconductor electronics were entirely based on germanium, although its production for such use today is a small fraction (2%) of that of ultra-high purity silicon, which has largely replaced it.

Germanium's major end uses in the present are fiber-optic systems and infrared optics. It is used in solar cell applications. Germanium compounds are used for polymerization catalysts. Germanium is finding a new use in nanowires. Germanium forms a large number of organometallic compounds, such as tetraethylgermane, which are useful in chemistry.

Germanium is not thought to be an essential element for any living organism. Some complexed organic germanium compounds are being investigated as possible pharmaceuticals but none has had success. Similar to silicon and aluminum, natural germanium compounds, which tend to be insoluble in water, have little oral toxicity. However, synthetic soluble germanium salts are nephrotoxic, and synthetic chemically reactive germanium compounds with halogens and hydrogen are irritants and toxins.

In his report on *The Periodic Law of the Chemical Elements*, in 1869, the Russian chemist Dmitri Ivanovich Mendeleev predicted the existence of several unknown chemical elements, including one that would fill a gap in the carbon family in his Periodic Table of the Elements, located between silicon and tin. Because of its position in his Periodic Table, Mendeleev called it *ekasilicon* (*Es*), and he estimated its atomic weight as about 72.0.

In mid-1885, at a mine near Freiberg, Saxony, a new mineral was discovered and named *argyrodite*, because of its high silver content. The chemist Clemens Winkler analyzed this new mineral, which proved to be a combination of silver, sulfur, and a new element. Winkler was able to isolate this new element and found it somewhat similar to antimony, in 1886. Before Winkler published his results on the new element, he decided that he would name his element *neptunium*, since the recent discovery of planet Neptune in 1846 had been preceded by mathematical predictions of its existence. However, the name "neptunium" had already been given to another chemical element (though not the element that today bears the name neptunium, which was discovered in 1940), so instead, Winkler named the new element *germanium* (from the Latin word, *Germania*, for Germany) in honor of his homeland. Argyrodite proved empirically to be Ag_8GeS_6 .

Because this new element showed some similarities with the elements arsenic and antimony, its proper place in the periodic table was under consideration, but its similarities with Dmitri Mendeleev's predicted element "ekasilicon" confirmed that it belonged in this place on the periodic table. With further material from 500 kg of ore from the mines in Saxony, Winkler confirmed the chemical properties of the new element in 1887. He also determined an atomic weight of 72.32 by analyzing pure germanium tetrachloride (GeCl_4), while Lecoq de Boisbaudran deduced 72.3 by a comparison of the lines in the spark spectrum of the element.

Winkler was able to prepare several new compounds of germanium, including its fluorides, chlorides, sulfides, germanium dioxide, and tetraethylgermane ($\text{Ge}(\text{C}_2\text{H}_5)_4$), the first organogermane. The physical data from these compounds — which corresponded well with Mendeleev's predictions — made the discovery an important confirmation of Mendeleev's idea of element periodicity.

Until the late 1930s, germanium was thought to be a poorly conducting metal. Germanium did not become economically significant until after 1945, when its properties as a semiconductor were recognized as being very useful in electronics.

However, during World War II, small amounts of germanium had begun to be used in some special electronic devices, mostly diodes. Its first major use was the point-contact Schottky diodes for radar pulse detection during the War. The first silicon-germanium alloys were obtained in 1955. Before 1945, only a few hundred kilograms of germanium were produced in smelters each year, but by the end of the 1950s, the annual worldwide production had reached 40 metric tons.

The development of the germanium transistor in 1948 opened the door to countless applications of solid state electronics. From 1950 through the early 1970s, this area provided an increasing market for germanium, but then high-purity silicon began replacing germanium in transistors, diodes, and rectifiers. For example, the company that became Fairchild Semiconductor was founded in 1957 with the express purpose of producing silicon transistors. Silicon has superior electrical properties, but it requires far higher purity, and this purity could not be commercially achieved in the early years of semiconductor electronics.

Meanwhile, the demand for germanium for use in fiber optics communication networks, infrared night vision systems, and polymerization catalysts increased dramatically. These end uses represented 85% of worldwide germanium consumption in 2000. The U.S. government even designated germanium as a strategic and critical material, calling for a 146 ton (132 t) supply in the national defense stockpile in 1987. Germanium differs from silicon in that the supply for germanium is limited by the availability of exploitable sources, while the supply of silicon is only limited by production capacity since silicon comes from ordinary sand or quartz.

Characteristics

Under standard conditions germanium is a brittle, silvery-white, semi-metallic element. This form constitutes an allotrope technically known as *α -germanium*, which has a metallic luster and a diamond cubic crystal structure, the same as diamond. At pressures above 120 kbar, a different allotrope known as *β -germanium* forms, which has the same structure as β -tin. Along with silicon, gallium, bismuth, antimony, and water, it is one of the few substances that expands as it solidifies (i.e. freezes) from its molten state.

Germanium is a semiconductor. Zone refining techniques have led to the production of crystalline germanium for semiconductors that has an impurity of only one part in 10^{10} , making it one of the purest materials ever obtained. The first metallic material discovered (in 2005) to become a superconductor in the presence of an extremely strong electromagnetic field was an alloy of germanium with uranium and rhodium.

Pure germanium is known to spontaneously extrude very long screw dislocations. They are one of the primary reasons for the failure of older diodes and transistors made from germanium; depending on what they eventually touch, they may lead to an electrical short.

Chemistry

Germanium is not thought to be essential to the health of plants or animals. Some of its compounds present a hazard to human health, however. For example, germanium chloride and germanium fluoride (GeF_4) are a liquid and gas, respectively that can be very irritating to the eyes, skin, lungs, and throat.

250 °C. Germanium is insoluble in dilute acids and alkalis but dissolves slowly in concentrated sulfuric acid and reacts violently with molten alkalis to produce germanates ($[\text{GeO}]^{2-3}$). Germanium occurs mostly in the oxidation state +4 although many compounds are known with the oxidation state of +2. Other oxidation states are rare, such as +3 found in compounds such as Ge_2Cl_6 , and +3 and +1 observed on the surface of oxides, or negative oxidation states in germanes, such as -4 in GeH_4 .

Germanium cluster anions (Zintl ions) such as Ge_4^{2-} , Ge_9^{4-} , Ge_9^{2-} , $[(\text{Ge}_9)_2]^{6-}$ have been prepared by the extraction from alloys containing alkali metals and germanium in liquid ammonia in the presence of ethylenediamine or a cryptand. The oxidation states of the element in these ions are not integers—similar to the ozonides O_3^- .

Two oxides of germanium are known: germanium dioxide (GeO_2 , germania) and germanium monoxide, (GeO). The dioxide, GeO_2 can be obtained by roasting germanium disulfide (GeS_2), and is a white powder that is only slightly soluble in water but reacts with alkalis to form germanates. The monoxide, germanous oxide, can be obtained by the high temperature reaction of GeO_2 with Ge metal. The dioxide (and the related oxides and germanates) exhibits the unusual property of having a high refractive index for visible light, but transparency to infrared light. Bismuth germanate, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, (BGO) is used as a scintillator.

Binary compounds with other chalcogens are also known, such as the disulfide (GeS_2), diselenide (GeSe_2), and the monosulfide (GeS), selenide (GeSe), and telluride (GeTe). GeS_2 forms as a white precipitate when hydrogen sulfide is passed through strongly acid solutions containing Ge(IV). The disulfide is appreciably soluble in water and in solutions of caustic alkalis or alkaline sulfides. Nevertheless, it is not soluble in acidic water, which allowed Winkler to discover the element. By heating the disulfide in a current of hydrogen, the monosulfide (GeS) is formed, which sublimes in thin plates of a dark color and metallic luster, and is soluble in solutions of the caustic alkalis. Upon melting with alkaline carbonates and sulfur, germanium compounds form salts known as thiogermanates.

Four tetrahalides are known. Under normal conditions GeI_4 is a solid, GeF_4 a gas and the others volatile liquids. For example, germanium tetrachloride, GeCl_4 , is obtained as a colorless fuming liquid boiling at 83.1 °C by heating the metal with chlorine. All the tetrahalides are readily hydrolyzed to hydrated germanium dioxide. GeCl_4 is used in the production of organogermanium compounds. All four dihalides are known and in contrast to the tetrahalides are polymeric solids. Additionally Ge_2Cl_6 and some higher compounds of formula $\text{Ge}_n\text{Cl}_{2n+2}$ are known. The unusual compound $\text{Ge}_6\text{Cl}_{16}$ has been prepared that contains the $\text{Ge}_5\text{Cl}_{12}$ unit with a neopentane structure.

Germane (GeH_4) is a compound similar in structure to methane. Polygermanes—compounds that are similar to alkanes—with formula $\text{Ge}_n\text{H}_{2n+2}$ containing up to five germanium atoms are known. The germanes are less volatile and less reactive than their corresponding silicon analogues. GeH_4 reacts with alkali metals in liquid ammonia to form white crystalline MGeH_3 which contain the GeH_3^- anion. The germanium hydrohalides with one, two and three halogen atoms are colorless reactive liquids.

The first organogermanium compound was synthesized by Winkler in 1887; the reaction of germanium tetrachloride with diethylzinc yielded tetraethylgermane ($\text{Ge}(\text{C}_2\text{H}_5)_4$). Organogermanes of the type R_4Ge (where R is an alkyl) such as tetramethylgermane ($\text{Ge}(\text{CH}_3)_4$) and tetraethylgermane are accessed through the cheapest available germanium precursor germanium tetrachloride and alkyl nucleophiles.

Organic germanium hydrides such as isobutylgermane ($(\text{CH}_3)_2\text{CHCH}_2\text{GeH}_3$) were found to be less hazardous and may be used as a liquid substitute for toxic germane gas in semiconductor applications. Many germanium reactive intermediates are known: germyl free radicals, germynes (similar to carbenes), and germynes (similar to carbynes). The organogermanium compound 2-carboxyethylgermasquioxane was first reported in the 1970s, and for a while was used as a dietary supplement and thought to possibly have anti-tumor qualities.

Applications

The major end uses for germanium in 2007, worldwide, were estimated to be: 35% for fiber-optic systems, 30% infrared optics, 15% for polymerization catalysts, and 15% for electronics and solar electric applications. The remaining 5% went into other uses such as phosphors, metallurgy, and chemotherapy.

Optics

The most notable physical characteristics of germania (GeO_2) are its high index of refraction and its low optical dispersion. These make it especially useful for wide-angle camera lenses, microscopy, and for the core part of optical fibers. It also replaced titania as the silica dopant for silica fiber, eliminating the need for subsequent heat treatment, which made the fibers brittle. At the end of 2002 the fiber optics industry accounted for 60% of the annual germanium use in the United States, but this use accounts for less than 10% of worldwide consumption. GeSbTe is a phase change material used for its optic properties, such as in rewritable DVDs.

Because germanium is transparent in the infrared it is a very important infrared optical material, that can be readily cut and polished into lenses and windows. It is especially used as the front optic in thermal imaging cameras working in the 8 to 14 micron wavelength range for passive thermal imaging and for hot-spot detection in military, night vision system in cars, and firefighting applications. It is therefore used in infrared spectrometers and other optical equipment which require extremely sensitive infrared detectors. The material has a very high refractive index (4.0) and so needs to be anti-reflection coated. Particularly, a very hard special antireflection coating of diamond-like carbon (DLC), refractive index 2.0, is a good match and produces a diamond-hard surface that can withstand much environmental rough treatment.

Electronics

Silicon-germanium alloys are rapidly becoming an important semiconductor material, for use in high-speed integrated circuits. Circuits utilizing the properties of Si-SiGe junctions can be much faster than those using silicon alone. Silicon-germanium is beginning to replace gallium arsenide (GaAs) in wireless communications devices. The SiGe chips, with high-speed properties, can be made with low-cost, well-established production techniques of the silicon chip industry.

The recent rise in energy cost has improved the economics of solar panels, a potential major new use of germanium. Germanium is the substrate of the wafers for high-efficiency multijunction photovoltaic cells for space applications.

Because germanium and gallium arsenide have very similar lattice constants, germanium substrates can be used to make gallium arsenide solar cells. The Mars Exploration Rovers and several satellites use triple junction gallium arsenide on germanium cells.

Germanium-on-insulator substrates are seen as a potential replacement for silicon on miniaturized chips. Other uses in electronics include phosphors in fluorescent lamps, and germanium-base solid-state light-emitting diodes (LEDs). Germanium transistors are still used in some effects pedals by musicians who wish to reproduce the distinctive tonal character of the "fuzz"-tone from the early rock and roll era.

Other Uses

Germanium dioxide is also used in catalysts for polymerization in the production of polyethylene terephthalate (PET). The high brilliance of the produced polyester is especially used for PET bottles marketed in Japan. However, in the United States, no germanium is used for polymerization catalysts. Due to the similarity between silica (SiO_2) and germanium dioxide (GeO_2), the silica stationary phase in some gas chromatography columns can be replaced by GeO_2 .

In recent years germanium has seen increasing use in precious metal alloys. In sterling silver alloys, for instance, it has been found to reduce firescale, increase tarnish resistance, and increase the alloy's response to precipitation hardening. A tarnish-proof sterling silver alloy, trademarked Argentium, requires 1.2% germanium.

High purity germanium single crystal detectors can precisely identify radiation sources—for example in airport security. Germanium is useful for monochromators for beamlines used in single crystal neutron scattering and synchrotron X-ray diffraction. The reflectivity has advantages over silicon in neutron and high energy X-ray applications. Crystals of high purity germanium are used in detectors for gamma spectroscopy and the search for dark matter.

Dietary Supplements, Pharmaceutical Development, and Health Hazard

Germanium is not thought to be essential to the health of plants or animals. Germanium in the environment has little or no health impact. This is primarily because it usually occurs only as a trace element in ores and carbonaceous materials, and is used in very small quantities that are not likely to be ingested, in its various industrial and electronic applications. For similar reasons, germanium in end-uses has little impact on the environment as a biohazard. Some reactive intermediate compounds of germanium are poisonous (see precautions, below).

Polonium- Metalloid

Polonium is a chemical element with the symbol **Po** and atomic number 84, discovered in 1898 by Marie and Pierre Curie. A rare and highly radioactive element with no stable isotopes, polonium is chemically similar to bismuth and tellurium, and it occurs in uranium ores. Applications of polonium are few, and include heaters in space probes, antistatic devices, and sources of neutrons and alpha particles. Because of its position in the periodic table, polonium is sometimes referred to as a metalloid, however others note that on the basis of its properties and behavior it is "unambiguously a metal".

Polonium is 'distinctly metallic' in some ways, or shows metallic character by way of:

- The metallic conductivity of both of its allotropic forms.
- The presence of the rose-colored Po^{2+} cation in aqueous solution.
- The many salts it forms.
- The predominating basicity of polonium dioxide.
- The highly reducing conditions required for the formation of the Po^{2-} anion in aqueous solution.



However, polonium shows nonmetallic character in that:

- Its halides have properties generally characteristic of nonmetal halides (being volatile, easily hydrolyzed, and soluble in organic solvents).
- Many metal polonides, obtained by heating the elements together at 500–1,000 °C, and containing the Po^{2-} anion, are also known.

Toxicity Overview

Polonium is highly dangerous and has no biological role. By mass, polonium-210 is around 250,000 times more toxic than hydrogen cyanide (the actual LD_{50} for ^{210}Po is less than 1 microgram for an average adult (see below) compared with about 250 milligrams for hydrogen cyanide). The main hazard is its intense radioactivity (as an alpha emitter), which makes it very difficult to handle safely. Even in microgram amounts, handling ^{210}Po is extremely dangerous, requiring specialized equipment (a negative pressure alpha glove box equipped with high performance filters), adequate monitoring, and strict handling procedures to avoid any contamination.

Alpha particles emitted by polonium will damage organic tissue easily if polonium is ingested, inhaled, or absorbed, although they do not penetrate the epidermis and hence are not hazardous as long as the alpha particles remain outside of the body. Meanwhile, wearing chemically resistant and "intact" gloves is a mandatory precaution to avoid transcutaneous diffusion of polonium directly through the skin. Polonium delivered in concentrated nitric acid can easily diffuse through inadequate gloves (e.g., latex gloves) or the acid may damage the gloves.

Acute Effects

The median lethal dose (LD₅₀) for acute radiation exposure is generally about 4.5 Sv. The committed effective dose equivalent ²¹⁰Po is 0.51 μSv/Bq if ingested, and 2.5 μSv/Bq if inhaled. Since ²¹⁰Po has an activity of 166 TBq per gram (4,500 Ci/g) (1 gram produces 166×10¹² decays per second), a fatal 4.5 Sv (J/kg) dose can be caused by ingesting 8.8 MBq (238 microcuries, μCi), about 50 nanograms (ng), or inhaling 1.8 MBq (48 μCi), about 10 ng. One gram of ²¹⁰Po could thus in theory poison 20 million people of whom 10 million would die.

The actual toxicity of ²¹⁰Po is lower than these estimates, because radiation exposure that is spread out over several weeks (the biological half-life of polonium in humans is 30 to 50 days) is somewhat less damaging than an instantaneous dose. It has been estimated that a median lethal dose of ²¹⁰Po is 0.015 GBq (0.4 mCi), or 0.089 micrograms, still an extremely small amount.

Long Term (Chronic) Effects

In addition to the acute effects, radiation exposure (both internal and external) carries a long-term risk of death from cancer of 5–10% per Sv. The general population is exposed to small amounts of polonium as a radon daughter in indoor air; the isotopes ²¹⁴Po and ²¹⁸Po are thought to cause the majority of the estimated 15,000–22,000 lung cancer deaths in the US every year that have been attributed to indoor radon. Tobacco smoking causes additional exposure to polonium.

Regulatory Exposure Limits and Handling

The maximum allowable body burden for ingested ²¹⁰Po is only 1.1 kBq (30 nCi), which is equivalent to a particle massing only 6.8 picograms. The maximum permissible workplace concentration of airborne ²¹⁰Po is about 10 Bq/m³ (3 × 10⁻¹⁰ μCi/cm³). The target organs for polonium in humans are the spleen and liver. As the spleen (150 g) and the liver (1.3 to 3 kg) are much smaller than the rest of the body, if the polonium is concentrated in these vital organs, it is a greater threat to life than the dose which would be suffered (on average) by the whole body if it were spread evenly throughout the body, in the same way as caesium or tritium (as T₂O).

²¹⁰Po is widely used in industry, and readily available with little regulation or restriction. In the US, a tracking system run by the Nuclear Regulatory Commission will be implemented in 2007 to register purchases of more than 16 curies (590 GBq) of polonium-210 (enough to make up 5,000 lethal doses). The IAEA "is said to be considering tighter regulations... There is talk that it might tighten the polonium reporting requirement by a factor of 10, to 1.6 curies (59 GBq)."

Polonium and its compounds must be handled in a glove box, which is further enclosed in another box, maintained at a slightly lower pressure than the glove box to prevent the radioactive materials from leaking out. Gloves made of natural rubber do not provide sufficient protection against the radiation from polonium; surgical gloves are necessary. Neoprene gloves shield radiation from polonium better than natural rubber.

Well-known Poisoning Cases

Notably, the murder of Alexander Litvinenko, a Russian dissident, in 2006 was announced as due to ²¹⁰Po poisoning (see Alexander Litvinenko poisoning). According to Prof. Nick Priest of Middlesex University, an environmental toxicologist and radiation expert, speaking on Sky News on December 2, Litvinenko was probably the first person ever to die of the acute α-radiation effects of ²¹⁰Po.

Silicon- Metalloid

Silicon is a tetravalent metalloid, is a chemical element with the symbol **Si** and atomic number 14. It is less reactive than its chemical analog carbon, the nonmetal directly above it in the periodic table, but more reactive than germanium, the metalloid directly below it in the table. Controversy about silicon's character dates to its discovery: silicon was first prepared and characterized in pure form in 1824, and given the name silicium (from Latin: *silicis*, flints), with an **-ium** word-ending to suggest a metal, a name which the element retains in several non-English languages. However, its final English name, suggested in 1831, reflects the more physically similar elements carbon and boron.

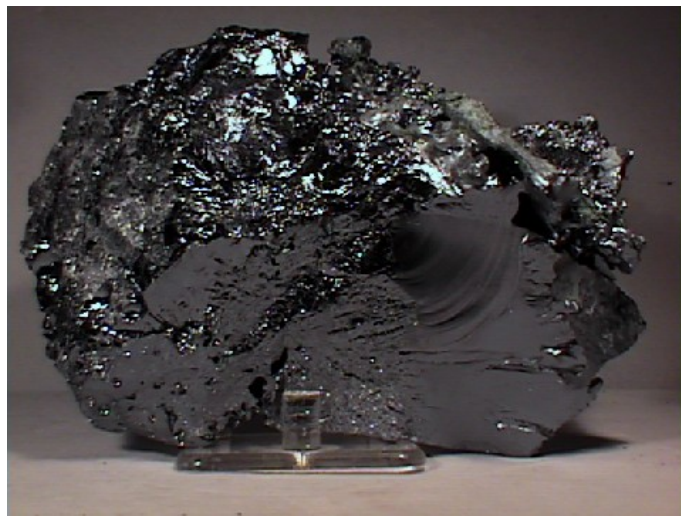
Silicon is the eighth most common element in the universe by mass, but very rarely occurs as the pure free element in nature. It is most widely distributed in dusts, sands, planetoids, and planets as various forms of silicon dioxide (silica) or silicates. Over 90% of the Earth's crust is composed of silicate minerals, making silicon the second most abundant element in the Earth's crust (about 28% by mass) after oxygen.

Most silicon is used commercially without being separated, and indeed often with little processing of compounds from nature. These include direct industrial building-use of clays, silica sand and stone. Silica is used in ceramic brick. Silicate goes into Portland cement for mortar and stucco, and when combined with silica sand and gravel, to make concrete. Silicates are also in whiteware ceramics such as porcelain, and in traditional quartz-based soda-lime glass. More modern silicon compounds such as silicon carbide form abrasives and high-strength ceramics. Silicon is the basis of the ubiquitous synthetic silicon-based polymers called silicones.

Elemental silicon also has a large impact on the modern world economy. Although most free silicon is used in the steel refining, aluminum-casting, and fine chemical industries (often to make fumed silica), the relatively small portion of very highly purified silicon that is used in semiconductor electronics (< 10%) is perhaps even more critical. Because of wide use of silicon in integrated circuits, the basis of most computers, a great deal of modern technology depends on it.

Silicon is an essential element in biology, although only tiny traces of it appear to be required by animals, however various sea sponges as well as microorganisms like diatoms need silicon in order to have structure. It is much more important to the metabolism of plants, particularly many grasses, and silicic acid (a type of silica) forms the basis of the striking array of protective shells of the microscopic diatoms.

Silicon is a solid at room temperature, with relatively high melting and boiling points of approximately 1,400 and 2,800 degrees Celsius respectively. Interestingly, silicon has a greater density in a liquid state than a solid state.



Therefore, it does not contract when it freezes like most substances, but expands, similar to how ice is less dense than water and has less mass per unit of volume than liquid water. With a relatively high thermal conductivity of $149 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, silicon conducts heat well and as a result is not often used to insulate hot objects.

In its crystalline form, pure silicon has a gray color and a metallic luster. Like germanium, silicon is rather strong, very brittle, and prone to chipping. Silicon, like carbon and germanium, crystallizes in a diamond cubic crystal structure, with a lattice spacing of approximately 0.5430710 nm (5.430710 Å).

The outer electron orbital of silicon, like that of carbon, has four valence electrons. The 1s, 2s, 2p and 3s subshells are completely filled while the 3p subshell contains two electrons out of a possible six.

Silicon is a semiconductor. It has a negative temperature coefficient of resistance, since the number of free charge carriers increases with temperature. The electrical resistance of single crystal silicon significantly changes under the application of mechanical stress due to the piezoresistive effect.

Isotopes of Silicon

Naturally occurring silicon is composed of three stable isotopes, silicon-28, silicon-29, and silicon-30, with silicon-28 being the most abundant (92% natural abundance). Out of these, only silicon-29 is of use in NMR and EPR spectroscopy. Twenty radioisotopes have been characterized, with the most stable being silicon-32 with a half-life of 170 years, and silicon-31 with a half-life of 157.3 minutes. All of the remaining radioactive isotopes have half-lives that are less than seven seconds, and the majority of these have half-lives that are less than one tenth of a second. Silicon does not have any known nuclear isomers.

The isotopes of silicon range in mass number from 22 to 44. The most common decay mode of six isotopes with mass numbers lower than the most abundant stable isotope, silicon-28, is Beta Positive β^+ , primarily forming aluminum isotopes (13 protons) as decay products. The most common decay mode(s) for 16 isotopes with mass numbers higher than silicon-28 is beta negative β^- , primarily forming phosphorus isotopes (15 protons) as decay products.

Occurrence

Measured by mass, silicon makes up 27.7% of the Earth's crust and is the second most abundant element in the crust, with only oxygen having a greater abundance. Silicon is usually found in the form of complex silicate minerals, and less often as silicon dioxide (**silica**, a major component of common sand). Pure silicon crystals are very rarely found in nature.

The silicate minerals—various minerals containing silicon, oxygen and reactive metals—account for 90% of the mass of the Earth's crust. This is due to the fact that at the high temperatures characteristic of the formation of the inner solar system, silicon and oxygen have a great affinity for each other, forming networks of silicon and oxygen in chemical compounds of very low volatility.

Since oxygen and silicon were the most common non-gaseous and non-metallic elements in the debris from supernova dust which formed the protoplanetary disk in the formation and evolution of the Solar System, they formed many complex silicates which accreted into larger rocky planetesimals that formed the terrestrial planets.

Here, the reduced silicate mineral matrix entrapped the metals reactive enough to be oxidized (aluminum, calcium, sodium, potassium and magnesium). After loss of volatile gases, as well as carbon and sulfur via reaction with hydrogen, this silicate mixture of elements formed most of the Earth's crust. These silicates were of relatively low density with respect to iron, nickel, and other metals non-reactive to oxygen and thus a residuum of uncombined iron and nickel sank to the planet's core, leaving a thick mantle consisting mostly of magnesium and iron silicates above.

Examples of silicate minerals in the crust include those in the pyroxene, amphibole, mica, and feldspar groups. These minerals occur in clay and various types of rock such as granite and sandstone.

Silica occurs in minerals consisting of very pure silicon dioxide in different crystalline forms, quartz, agate amethyst, rock crystal, chalcedony, flint, jasper, and opal. The crystals have the empirical formula of silicon dioxide, but do not consist of separate silicon dioxide molecules in the manner of solid carbon dioxide. Rather, silica is structurally a network-solid consisting of silicon and oxygen in three-dimensional crystals, like diamond. Less pure silica forms the natural glass obsidian. Biogenic silica occurs in the structure of diatoms, radiolaria and siliceous sponges.

Silicon is also a principal component of many meteorites, and is a component of tektites, a silicate mineral of possibly lunar origin, or (if Earth-derived) which has been subjected to unusual temperatures and pressures, possibly from meteorite strike.

Production

Alloys

Ferrosilicon, an iron-silicon alloy that contains varying ratios of elemental silicon and iron, accounts for about 80% of the world's production of elemental silicon, with China, the leading supplier of elemental silicon, providing 4.6 million tons (or 2/3 of the world output) of silicon, most of which is in the form of ferrosilicon. It is followed by Russia (610,000 t), Norway (330,000 t), Brazil (240,000 t) and the United States (170,000 t). Ferrosilicon is primarily used by the steel industry (see below).

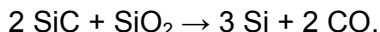
Aluminum-silicon alloys are heavily used in the aluminum alloy casting industry, where silicon is the single most important additive to aluminum to improve its casting properties. Since cast aluminum is widely used in the automobile industry, this use of silicon is thus the single largest industrial use of "metallurgical grade" pure silicon (as this purified silicon is added to pure aluminum, whereas ferrosilicon is never purified before being added to steel).

Metallurgical Grade

Elemental silicon not alloyed with significant quantities of other elements, and usually > 95%, is often referred to loosely as silicon metal. It makes up about 20% of the world total elemental silicon production, with less than 1 to 2% of total elemental silicon (5–10% of metallurgical grade silicon) ever purified to higher grades for use in electronics. Metallurgical grade silicon is commercially prepared by the reaction of high-purity silica with wood, charcoal, and coal in an electric arc furnace using carbon electrodes. At temperatures over 1,900 °C (3,450 °F), the carbon in the aforementioned materials and the

silicon undergo the chemical reaction $\text{SiO}_2 + 2 \text{C} \rightarrow \text{Si} + 2 \text{CO}$. Liquid silicon collects in the bottom of the furnace, which is then drained and cooled.

The silicon produced this manner is called *metallurgical grade silicon* and is at least 98% pure. Using this method, silicon carbide (SiC) may also form from an excess of carbon in one or both of the following ways: $\text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO}$ or $\text{SiO} + 2 \text{C} \rightarrow \text{SiC} + \text{CO}$. However, provided the concentration of SiO_2 is kept high, the silicon carbide can be eliminated by the chemical reaction



As noted above, metallurgical grade silicon "metal" has its primary use in the aluminum casting industry to make aluminum-silicon alloy parts. The remainder (about 45%) is used by the chemical industry, where it is primarily employed to make fumed silica.

Electronic Grade

The use of silicon in semiconductor devices demands a much greater purity than afforded by metallurgical grade silicon. Very pure silicon (>99.9%) can be extracted directly from solid silica or other silicon compounds by molten salt electrolysis. This method, known as early as 1854 (see also FFC Cambridge process), has the potential to directly produce solar-grade silicon without any carbon dioxide emission at much lower energy consumption.

Solar grade silicon cannot be used for semiconductors, where purity must be extreme to properly control the process. Bulk silicon wafers used at the beginning of the integrated circuit making process must first be refined to "nine nines" purity (99.999999%), a process which requires repeated applications of refining technology.

The majority of silicon crystals grown for device production are produced by the Czochralski process, (CZ-Si) since it is the cheapest method available and it is capable of producing large size crystals. However, single crystals grown by the Czochralski process contain impurities because the crucible containing the melt often dissolves. Historically, a number of methods have been used to produce ultra-high-purity silicon.

Early silicon purification techniques were based on the fact that if silicon is melted and re-solidified, the last parts of the mass to solidify contain most of the impurities. The earliest method of silicon purification, first described in 1919 and used on a limited basis to make radar components during World War II, involved crushing metallurgical grade silicon and then partially dissolving the silicon powder in an acid. When crushed, the silicon cracked so that the weaker impurity-rich regions were on the outside of the resulting grains of silicon. As a result, the impurity-rich silicon was the first to be dissolved when treated with acid, leaving behind a more pure product.

In zone melting, also called zone refining, the first silicon purification method to be widely used industrially, rods of metallurgical grade silicon are heated to melt at one end. Then, the heater is slowly moved down the length of the rod, keeping a small length of the rod molten as the silicon cools and re-solidifies behind it.

Since most impurities tend to remain in the molten region rather than re-solidify, when the process is complete, most of the impurities in the rod will have been moved into the end that was the last to be melted. This end is then cut off and discarded, and the process repeated if a still higher purity is desired.

At one time, DuPont produced ultra-pure silicon by reacting silicon tetrachloride with high-purity zinc vapors at 950 °C, producing silicon by $\text{SiCl}_4 + 2 \text{Zn} \rightarrow \text{Si} + 2 \text{ZnCl}_2$. However, this technique was plagued with practical problems (such as the zinc chloride byproduct solidifying and clogging lines) and was eventually abandoned in favor of the Siemens process. In the *Siemens process*, high-purity silicon rods are exposed to trichlorosilane at 1150 °C. The trichlorosilane gas decomposes and deposits additional silicon onto the rods, enlarging them because $2 \text{HSiCl}_3 \rightarrow \text{Si} + 2 \text{HCl} + \text{SiCl}_4$. Silicon produced from this and similar processes is called *polycrystalline silicon*. Polycrystalline silicon typically has impurity levels of less than one part per billion.

In 2006 REC announced construction of a plant based on *fluidized bed* (FB) technology using silane: $3 \text{SiCl}_4 + \text{Si} + 2 \text{H}_2 \rightarrow 4 \text{HSiCl}_3$, $4 \text{HSiCl}_3 \rightarrow 3 \text{SiCl}_4 + \text{SiH}_4$, $\text{SiH}_4 \rightarrow \text{Si} + 2 \text{H}_2$. The advantage of fluid bed technology is that processes can be run continuously, yielding higher yields than Siemens Process, which is a batch process.

Today, silicon is purified by converting it to a silicon compound that can be more easily purified by distillation than in its original state, and then converting that silicon compound back into pure silicon. Trichlorosilane is the silicon compound most commonly used as the intermediate, although silicon tetrachloride and silane are also used. When these gases are blown over silicon at high temperature, they decompose to high-purity silicon.

In addition, there is the *Schumacher process*, which utilizes tribromosilane in place of trichlorosilane and fluid bed technology. It requires lower deposition temperatures, lower capital costs to build facilities and operate, no hazardous polymers nor explosive material, and produces no amorphous silicon dust waste, all of which are drawbacks of the Siemens process. However, there are yet to be any major factories built using this process.

Compounds

- Silicon forms binary compounds called silicides with many metallic elements whose properties range from reactive compounds, e.g. magnesium silicide, Mg_2Si through high melting refractory compounds such as molybdenum disilicide, MoSi_2 .
- Silicon carbide, SiC (carborundum) is a hard, high melting solid and a well-known abrasive. It may also be sintered into a type of high-strength ceramic used in armor.
- Silane, SiH_4 , is a pyrophoric gas with a similar tetrahedral structure to methane, CH_4 . When pure, it does not react with pure water or dilute acids; however, even small amounts of alkali impurities from the laboratory glass can result in a rapid hydrolysis. There is a range of catenated silicon hydrides that form a homologous series of compounds, $\text{Si}_n\text{H}_{2n+2}$ where $n = 2-8$ (analogous to the alkanes). These are all readily hydrolyzed and are thermally unstable, particularly the heavier members.
- Disilenes contain a silicon-silicon double bond (analogous to the alkenes) and are generally highly reactive requiring large substituent groups to stabilize them. A disilyne with a silicon-silicon triple bond was first isolated in 2004; although as the compound is non-linear, the bonding is dissimilar to that in alkynes.
- Tetrahalides, SiX_4 , are formed with all the halogens. Silicon tetrachloride, for example, reacts with water, unlike its carbon analogue, carbon tetrachloride. Silicon dihalides are formed by the high temperature reaction of tetrahalides and silicon;

with a structure analogous to a carbene they are reactive compounds. Silicon difluoride condenses to form a polymeric compound, $(\text{SiF}_2)_n$.

- Silicon dioxide is a high melting solid with a number of crystal forms; the most familiar of which is the mineral quartz. In quartz each silicon atom is surrounded by four oxygen atoms that bridge to other silicon atoms to form a three dimensional lattice. Silica is soluble in water at high temperatures forming a range of compounds called *monosilicic acid*, $\text{Si}(\text{OH})_4$.
- Under the right conditions monosilicic acid readily polymerizes to form more complex silicic acids, ranging from the simplest condensate, disilicic acid ($\text{H}_6\text{Si}_2\text{O}_7$) to linear, ribbon, layer and lattice structures which form the basis of the many silicate minerals and are called *polysilicic acids* $\{\text{Si}_x(\text{OH})_{4-2x}\}_n$.
- With oxides of other elements the high temperature reaction of silicon dioxide can give a wide range of glasses with various properties. Examples include soda lime glass, borosilicate glass and lead crystal glass.
- Silicon sulfide, SiS_2 is a polymeric solid (unlike its carbon analogue the liquid CS_2).
- Silicon forms a nitride, Si_3N_4 which is a ceramic. Silatranes, a group of tricyclic compounds containing five-coordinate silicon, may have physiological properties.
- Many transition metal complexes containing a metal-silicon bond are now known, which include complexes containing $\text{SiH}_n\text{X}_{3-n}$ ligands, SiX_3 ligands, and $\text{Si}(\text{OR})_3$ ligands.
- Silicones are large group of polymeric compounds with an (Si-O-Si) backbone. An example is the silicone oil PDMS (polydimethylsiloxane). These polymers can be crosslinked to produce resins and elastomers.
- Many organosilicon compounds are known which contain a silicon-carbon single bond. Many of these are based on a central tetrahedral silicon atom, and some are optically active when central chirality exists. Long chain polymers containing a silicon backbone are known, such as polydimethylsilylene $(\text{SiMe}_2)_n$. Polycarbosilane, $[(\text{SiMe}_2)_2\text{CH}_2]_n$ with a backbone containing a repeating -Si-Si-C unit, is a precursor in the production of silicon carbide fibers.

History

Attention was first drawn to quartz as the possible oxide of a fundamental chemical element by Antoine Lavoisier, in 1787. In 1811, Gay-Lussac and Thénard are thought to have prepared impure amorphous silicon, through the heating of recently isolated potassium metal with silicon tetrafluoride, but they did not purify and characterize the product, nor identify it as a new element. In 1824, Berzelius prepared amorphous silicon using approximately the same method as Gay-Lussac (potassium metal and potassium fluorosilicate), but purifying the product to a brown powder by repeatedly washing it. He named the product *silicium* from the Latin *silix*, *silicis* for flint, flints, and adding the "-ium" ending because he believed it was a metal. As a result he is usually given credit for the element's discovery. Silicon was given its present name in 1831 by Scottish chemist Thomas Thomson. He retained part of Berzelius's name but added "-on" because he believed silicon a nonmetal more similar to boron and carbon.

Tellurium- Metalloid

Tellurium is a chemical element with symbol Te and atomic number 52. A brittle, mildly toxic, rare, silver-white metalloid which looks similar to tin, tellurium is chemically related to selenium and sulfur. It is occasionally found in native form, as elemental crystals. Tellurium is far more common in the universe as a whole than it is on Earth. Its extreme rarity in the Earth's crust, comparable to that of platinum, is partly due to its high atomic number, but also due to its formation of a volatile hydride which caused the element to be lost to space as a gas during the hot nebular formation of the planet.

Tellurium was discovered in Transylvania (today part of Romania) in 1782 by Franz-Joseph Müller von Reichenstein in a mineral containing tellurium and gold. Martin Heinrich Klaproth named the new element in 1798 after the Latin word for "earth", *tellus*. Gold telluride minerals are the most notable natural gold compounds. However, they are not a commercially significant source of tellurium itself, which is normally extracted as a by-product of copper and lead production.



Commercially, the primary use of tellurium is in alloys, foremost in steel and copper to improve machinability. Applications in solar panels and as a semiconductor material also consume a considerable fraction of tellurium production.

Tellurium has no biological function, although fungi can incorporate it in place of sulfur and selenium into amino acids such as tellurocysteine and telluromethionine. In humans, tellurium is partly metabolized into dimethyl telluride, $(\text{CH}_3)_2\text{Te}$, a gas with a garlic-like odor which is exhaled in the breath of victims of tellurium toxicity or exposure.

Characteristics

Physical Properties

When crystalline, tellurium is silvery-white and when it is in pure state it has a metallic luster. It is a brittle and easily pulverized metalloid. Amorphous tellurium is found by precipitating it from a solution of tellurous or telluric acid $\text{Te}(\text{OH})_6$. Tellurium is a semiconductor that shows a greater electrical conductivity in certain directions which depends on atomic alignment; the conductivity increases slightly when exposed to light (photoconductivity). When in its molten state, tellurium is corrosive to copper, iron and stainless steel.

Chemical Properties

Tellurium adopts a polymeric structure, consisting of zig-zag chains of Te atoms. This gray material resists oxidation by air and is nonvolatile.

Isotopes

Naturally occurring tellurium has eight isotopes. Five of those isotopes, ^{122}Te , ^{123}Te , ^{124}Te , ^{125}Te and ^{126}Te , are stable. The other three, ^{120}Te , ^{128}Te and ^{130}Te , have been observed to be radioactive. The stable isotopes make up only 33.2% of the naturally occurring tellurium; this is possible due to the long half-lives of the unstable isotopes. They are in the range from 10^{13} to 2.2×10^{24} years (for ^{128}Te).

This makes ^{128}Te the isotope with the longest half-life among all radionuclides, which is approximately 160 trillion (10^{12}) times the age of known universe.

There are 38 known nuclear isomers of tellurium with atomic masses that range from 105 to 142. Tellurium is among the lightest elements known to undergo alpha decay, with isotopes ^{106}Te to ^{110}Te being able to undergo this mode of decay.^[6] The atomic mass of tellurium ($127.60\text{ g}\cdot\text{mol}^{-1}$) exceeds that of the following element iodine ($126.90\text{ g}\cdot\text{mol}^{-1}$).

Occurrence

With an abundance in the Earth's crust comparable to that of platinum, tellurium is one of the rarest stable solid elements in the Earth's crust. Its abundance is about $1\text{ }\mu\text{g/kg}$. In comparison, even the rarest of the lanthanides have crustal abundances of $500\text{ }\mu\text{g/kg}$ (see Abundance of the chemical elements).

The extreme rarity of tellurium in the Earth's crust is not a reflection of its cosmic abundance, which is in fact greater than that of rubidium, even though rubidium is ten thousand times more abundant in the Earth's crust. The extraordinarily low abundance of tellurium on Earth is rather thought to be due to conditions in the Earth's formation, when the stable form of certain elements, in the absence of oxygen and water, was controlled by the reductive power of free hydrogen. Under this scenario, certain elements such as tellurium which form volatile hydrides were severely depleted during the formation of the Earth's crust, through evaporation of these hydrides. Tellurium and selenium are the heavy elements most depleted in the Earth's crust by this process.

Tellurium is sometimes found in its native (i.e., elemental) form, but is more often found as the tellurides of gold such as calaverite and krennerite (two different polymorphs of AuTe_2), petzite, Ag_3AuTe_2 , and sylvanite, AgAuTe_4 . The city of Telluride, Colorado was named in hope of a strike of gold telluride (which never materialized, though gold metal ore was found). Gold itself is usually found uncombined, but when found naturally as a chemical compound, it is most often combined with tellurium (a few rare non-telluride gold compounds such as the antimonide aurostibite, AuSb_2 , and bismuthide maldonite, Au_2Bi , are also known).

Although tellurium is found with gold more often than in uncombined form, it is found even more often combined with elements other than gold, as tellurides more common metals (e.g. melonite, NiTe_2). Natural tellurite and tellurate minerals also occur, formed by oxidation of tellurides near the Earth's surface. In contrast to selenium, tellurium is not in general able to replace sulfur in its minerals, due to the large difference in ion radius of sulfur and tellurium. In consequence, many common sulfide minerals contain considerable amounts of selenium, but only traces of tellurium.

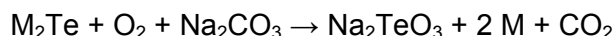
In the gold rush of 1893, diggers in Kalgoorlie discarded a pyritic material which got in their way as they searched for pure gold. The Kalgoorlie waste was thus used to fill in potholes or as part of sidewalks. Three years passed before it was realized that this waste was calaverite, a telluride of gold that had not been recognized. This led to a second gold rush in 1896 which included mining the streets.

Production

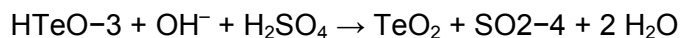
The principal source of tellurium is from anode sludges produced during the electrolytic refining of blister copper. It is a component of dusts from blast furnace refining of lead. Treatment of 500 tons of copper ore typically yields one pound (0.45 kg) of tellurium. Tellurium is produced mainly in the United States, Peru, Japan and Canada.

For the year 2009 the British Geological Survey gives the following numbers: United States 50 t, Peru 7 t, Japan 40 t and Canada 16 t. The anode sludges contain the selenides and tellurides of the noble metals in compounds with the formula M_2Se or M_2Te ($M = Cu, Ag, Au$). At temperatures of 500 °C the anode sludges are roasted with sodium carbonate under air.

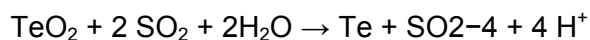
The metal ions are reduced to the metals, while the telluride is converted to sodium tellurite.



Tellurites can be leached from the mixture with water and are normally present as hydrotellurites $HTeO_3^-$ in solution. Selenites are also formed during this process, but they can be separated by adding sulfuric acid. The hydrotellurites are converted into the insoluble tellurium dioxide while the selenites stay in solution.



The reduction to the metal is done either by electrolysis or by reacting the tellurium dioxide with sulfur dioxide in sulfuric acid.



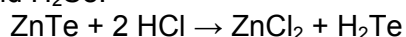
Commercial-grade tellurium is usually marketed as 200-mesh powder but is also available as slabs, ingots, sticks, or lumps. The year-end price for tellurium in 2000 was US\$14 per pound. In recent years, the tellurium price was driven up by increased demand and limited supply, reaching as high as US\$100 per pound in 2006. Despite an expected doubling in production due to improved extraction methods, the United States Department of Energy (DoE) anticipates a supply shortfall of tellurium by 2025.

Compounds

Tellurium belongs to the same chemical family as oxygen, sulfur, selenium and polonium: the chalcogen family. Tellurium and selenium compounds are similar. It exhibits the oxidation states -2, +2, +4 and +6, with the +4 state being most common.

Tellurides

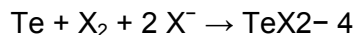
Reduction of Te metal produces the tellurides and polytellurides, Te_n^{2-} . The -2 oxidation state is exhibited in binary compounds with many metals, such as zinc telluride, $ZnTe$, formed by heating tellurium with zinc. Decomposition of $ZnTe$ with hydrochloric acid yields hydrogen telluride (H_2Te), a highly unstable analogue of the other chalcogen hydrides, H_2O , H_2S and H_2Se :



H_2Te is unstable, whereas salts of its conjugate base $[TeH]^-$ are stable.

Halides

The +2 oxidation state is exhibited by the dihalides, TeCl_2 , TeBr_2 and TeI_2 . The dihalides have not been obtained in pure form, although they are known decomposition products of the tetrahalides in organic solvents, and their derived tetrahalotellurates are well-characterized:



where X is Cl, Br, or I. These anions are square planar in geometry. Polynuclear anionic species also exist, such as the dark brown $\text{Te}_2\text{I}_2^{2-}$, and the black $\text{Te}_4\text{I}_2^{14-}$.

Fluorine forms two halides with tellurium: the mixed-valence Te_2F_4 and TeF_6 . In the +6 oxidation state, the $-\text{OTeF}_5$ structural group occurs in a number of compounds such as HOTeF_5 , $\text{B}(\text{OTeF}_5)_3$, $\text{Xe}(\text{OTeF}_5)_2$, $\text{Te}(\text{OTeF}_5)_4$ and $\text{Te}(\text{OTeF}_5)_6$. The square antiprismatic anion TeF_2^{8-} is also attested. The other halogens do not form halides with tellurium in the +6 oxidation state, but only tetrahalides (TeCl_4 , TeBr_4 and TeI_4) in the +4 state, and other lower halides (Te_3Cl_2 , Te_2Cl_2 , Te_2Br_2 , Te_2I and two forms of TeI). In the +4 oxidation state, halotellurate anions are known, such as TeCl_2^{6-} and $\text{Te}_2\text{Cl}_2^{10-}$.

Halotellurium cations are also attested, including TeI^{3+} , found in TeI_3AsF_6 .

Oxocompounds

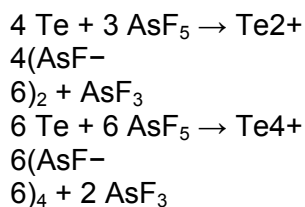
Tellurium monoxide was first reported in 1883 as a black amorphous solid formed by the heat decomposition of TeSO_3 in vacuum, disproportionating into tellurium dioxide, TeO_2 and elemental tellurium upon heating. Since then, however, some doubt has been cast on its existence in the solid phase, although it is known as a vapor phase fragment; the black solid may be merely an equimolar mixture of elemental tellurium and tellurium dioxide.

Tellurium dioxide is formed by heating tellurium in air, causing it to burn with a blue flame. Tellurium trioxide, $\beta\text{-TeO}_3$, is obtained by thermal decomposition of $\text{Te}(\text{OH})_6$. The other two forms of trioxide reported in the literature, the α - and γ - forms, were found not to be true oxides of tellurium in the +6 oxidation state, but a mixture of Te^{4+} , OH^- and O^{2-} . Tellurium also exhibits mixed-valence oxides, Te_2O_5 and Te_4O_9 .

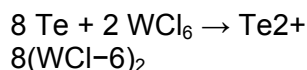
The tellurium oxides and hydrated oxides form a series of acids, including tellurous acid (H_2TeO_3), orthotelluric acid ($\text{Te}(\text{OH})_6$) and metatelluric acid ($(\text{H}_2\text{TeO}_4)_n$). The two forms of telluric acid form *tellurate* salts containing the TeO_2^{4-} and TeO_6^{6-} anions, respectively. Tellurous acid forms *tellurite* salts containing the anion TeO_2^{3-} . Other tellurium cations include TeF_2^{8+} , which consists of two fused tellurium rings and the polymeric TeF_2^{7+} .

Zintl cations

When tellurium is treated with concentrated sulfuric acid, it forms red solutions containing the Zintl ion, Te_2^{+4} . The oxidation of tellurium by AsF_5 in liquid SO_2 also produces this square planar cation, as well as with the trigonal prismatic, yellow-orange Te_4^{+6} :



Other tellurium Zintl cations include the polymeric Te_2^{+7} and the blue-black Te_2^{+8} , which consists of two fused 5-membered tellurium rings. The latter cation is formed by the reaction of tellurium with tungsten hexachloride:



Interchalcogen cations also exist, such as $\text{Te}_2\text{Se}_2^{+6}$ (distorted cubic geometry) and $\text{Te}_2\text{Se}_2^{+8}$. These are formed by oxidizing mixtures of tellurium and selenium with AsF_5 or SbF_5 .

Organotellurium compounds

Tellurium does not readily form analogues of alcohols and thiols, with the functional group $-\text{TeH}$ and are called tellurols. The $-\text{TeH}$ functional group is also attributed to using the prefix *tellanyl-*. Like H_2Te , these species are unstable with respect to loss of hydrogen. Telluraethers ($\text{R}-\text{Te}-\text{R}$) are more stable as are telluroxides.

History

from the mines in Zlatna, near what is now Sibiu, Transylvania. This ore was known as "Faczebajer weißes blättriges Golderz" (white leafy gold ore from Faczebaja) or *antimonialischer Goldkies* (antimonic gold pyrite), and, according to Anton von Rupprecht, was *Spießglaskönig* (*argent molybdique*), containing native antimony. In 1782 Franz-Joseph Müller von Reichenstein, who was then serving as the Austrian chief inspector of mines in Transylvania, concluded that the ore did not contain antimony, but that it was bismuth sulfide.

The following year, he reported that this was erroneous and that the ore contained mostly gold and an unknown metal very similar to antimony. After a thorough investigation which lasted for three years and consisted of more than fifty tests, Müller determined the specific gravity of the mineral and noted the radish-like odor of the white smoke which passed off when the new metal was heated, the red color which the metal imparts to sulfuric acid, and the black precipitate which this solution gives when diluted with water. Nevertheless, he was not able to identify this metal and gave it the names *aurum paradoxium* and *metallum problematicum*, as it did not show the properties predicted for the expected antimony.

In 1789, another Hungarian scientist, Pál Kitaibel, also discovered the element independently in an ore from Deutsch-Pilsen which had been regarded as argentiferous molybdenite, but later he gave the credit to Müller. In 1798, it was named by Martin Heinrich Klaproth who earlier isolated it from the mineral calaverite. The 1960s brought growth in thermoelectric applications for tellurium (as bismuth telluride), as well as its use in free-machining steel, which became the dominant use.

Applications

Metallurgy

The largest consumer of tellurium is metallurgy, where it is used in iron, copper and lead alloys. When added to stainless steel and copper it makes these metals more machinable. It is alloyed into cast iron for promoting chill for spectroscopic purposes, as the presence of electrically conductive free graphite tends to deleteriously affect spark emission testing results. In lead it improves strength and durability and decreases the corrosive action of sulfuric acid.

Semiconductor and electronics industry uses

Tellurium is used in cadmium telluride (CdTe) solar panels. National Renewable Energy Laboratory lab tests using this material achieved some of the highest efficiencies for solar cell electric power generation. Massive commercial production of CdTe solar panels by First Solar in recent years has significantly increased tellurium demand. If some of the cadmium in CdTe is replaced by zinc then (Cd,Zn)Te is formed which is used in solid-state X-ray detectors.

Alloyed with both cadmium and mercury, to form mercury cadmium telluride, an infrared sensitive semiconductor material is formed. Organotellurium compounds such as dimethyl telluride, diethyl telluride, diisopropyl telluride, diallyl telluride and methyl allyl telluride are used as precursors for metalorganic vapor phase epitaxy growth of II-VI compound semiconductors. Diisopropyl telluride (DIPTe) is employed as the preferred precursor for achieving the low-temperature growth of CdHgTe by MOVPE. For these processes highest purity metalorganics of both selenium and tellurium are used. The compounds for semiconductor industry and are prepared by adduct purification.

Tellurium as a tellurium suboxide is used in the media layer of several types of rewritable optical discs, including ReWritable Compact Discs (CD-RW), ReWritable Digital Video Discs (DVD-RW) and ReWritable Blu-ray Discs. Tellurium is used in the new phase change memory chips developed by Intel. Bismuth telluride (Bi_2Te_3) and lead telluride are working elements of thermoelectric devices. Lead telluride is used in far-infrared detectors.

Other Uses

- Used to color ceramics.
- The strong increase in optical refraction upon the addition of selenides and tellurides into glass is used in the production of glass fibers for telecommunications. These chalcogenide glasses are widely used.
- Mixtures of selenium and tellurium are used with barium peroxide as oxidizer in the delay powder of electric blasting caps.
- Organic tellurides have been employed as initiators for living radical polymerization and electron-rich mono- and di-tellurides possess antioxidant activity.

Allotropes Section

Allotropy or allotropism is the property of some chemical elements to exist in two or more different forms, known as allotropes of these elements. Allotropes are different structural modifications of an element; the atoms of the element are bonded together in a different manner.

For example, the allotropes of carbon include diamond (where the carbon atoms are bonded together in a tetrahedral lattice arrangement), graphite (where the carbon atoms are bonded together in sheets of a hexagonal lattice), graphene (single sheets of graphite), and fullerenes (where the carbon atoms are bonded together in spherical, tubular, or ellipsoidal formations).

The term allotropy is used for elements only, not for compounds. The more general term, used for any crystalline material, is polymorphism. Allotropy refers only to different forms of an element within the same phase (i.e. different solid, liquid or gas forms); the changes of state between solid, liquid and gas in themselves are not considered allotropy.

For some elements, allotropes have different molecular formulae which can persist in different phases – for example, two allotropes of oxygen (dioxygen, O₂ and ozone, O₃), can both exist in the solid, liquid and gaseous states. Conversely, some elements do not maintain distinct allotropes in different phases – for example phosphorus has numerous solid allotropes, which all revert to the same P₄ form when melted to the liquid state.

The concept of allotropy was originally proposed in 1841 by the Swedish scientist Baron Jöns Jakob Berzelius (1779–1848). The term is derived from the Greek *ἀλλοτροπία* (*allotropia*; variability, changeableness). After the acceptance of Avogadro's hypothesis in 1860 it was understood that elements could exist as polyatomic molecules, and the two allotropes of oxygen were recognized as O₂ and O₃. In the early 20th century it was recognized that other cases such as carbon were due to differences in crystal structure.

By 1912, Ostwald noted that the allotropy of elements is just a special case of the phenomenon of polymorphism known for compounds, and proposed that the terms allotrope and allotropy be abandoned and replaced by polymorph and polymorphism. Although many other chemists have repeated this advice, IUPAC and most chemistry texts still favor the usage of allotrope and allotropy for elements only.

List of Allotropes

Typically, elements capable of variable coordination number and/or oxidation states tend to exhibit greater numbers of allotropic forms. Another contributing factor is the ability of an element to catenate. Allotropes are typically more noticeable in non-metals (excluding the halogens and the noble gases) and metalloids. Nevertheless, metals tend to have many allotropes.



Cerium, left, Dysprosium, right.

Examples of allotropes include:

Non-metals

Element	Allotropes
Carbon	• Diamond - an extremely hard, transparent crystal, with the carbon atoms arranged in a tetrahedral lattice. A poor electrical conductor. An excellent thermal conductor. • Lonsdaleite - also called hexagonal diamond. • Graphite - a soft, black, flaky solid, a moderate electrical conductor. The C atoms are bonded in flat hexagonal lattices (graphene), which are then layered in sheets.
	• Linear acetylenic carbon (Carbyne) • Amorphous carbon • Fullerenes, including Buckminsterfullerene, aka "buckyballs", such as C₆₀. • Carbon nanotubes - allotropes of carbon with a cylindrical nanostructure.
	• White phosphorus - crystalline solid P₄ • Red phosphorus - polymeric solid • Scarlet phosphorus
	• Violet phosphorus • Black phosphorus - semiconductor, analogous to graphite • Diphosphorus
Oxygen:	• dioxygen, O₂ - colorless (faint blue) • Ozone, O₃ - blue
	• Tetraoxygen, O₄ - metastable • Octaoxygen, O₈ - red
	• Sulfur has a large number of allotropes, second only to carbon
Sulfur:	• "Red selenium," cyclo-Se₈
	• Gray selenium, polymeric Se
Selenium:	

Metalloids
Element

Allotropes

- Amorphous boron - brown powder - B₁₂ regular icosahedra
- α-rhombohedral boron
- β-rhombohedral boron
- Boron:
 - γ-orthorhombic boron
 - α-tetragonal boron
 - β-tetragonal boron
 - High-pressure superconducting phase
- Amorphous silicon
- Silicon:
 - crystalline silicon, Diamond cubic structure
- Yellow arsenic - molecular non-metallic As₄, with the same structure of white phosphorus
- Arsenic:
 - Gray arsenic, polymeric As (metalloid)
 - Black arsenic - molecular and non-metallic, with the same structure of red phosphorus
- α-germanium – semi-metallic, with the same structure of diamond
- Germanium:
 - β-germanium - metallic, with the same structure of beta-tin
- blue-white antimony - the stable form (metalloid)
- yellow antimony (non-metallic)
- Antimony:
 - black antimony (non-metallic)
 - explosive antimony
- α-polonium - simple cubic (metallic)
- Polonium:
 - β-polonium - rhombohedral (metallic)

Metals

Among the metallic elements that occur in nature in significant quantities (up to U, without Tc and Pm), 27 are allotropic at ambient pressure: Li, Be, Na, Ca, Ti, Mn, Fe, Co, Sr, Y, Zr, Sn, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Yb, Hf, Ta, Th, Pa and U. Some phase transitions between allotropic forms of technologically-relevant metals are those of Ti at 882°C, Fe at 912°C and 1394°C, Co at 422°C, Zr at 863°C, Sn at 13°C and U at 668°C and 776°C.

Element Allotropes

- | | |
|-------|---|
| | <ul style="list-style-type: none">• grey tin (alpha tin)• white tin (beta tin) |
| Tin: | <ul style="list-style-type: none">• rhombic tin (gamma tin)• sigma tin |
| | <ul style="list-style-type: none">• ferrite (alpha iron) - forms below 770°C (the Curie point, T_C); the iron becomes magnetic in its alpha form; BCC• beta - forms below 912°C ; BCC crystal structure |
| Iron: | <ul style="list-style-type: none">• gamma - forms below 1,394°C; FCC crystal structure• delta - forms from cooling down molten iron below 1,538°C; BCC crystal structure• epsilon - forms at high pressures |

Lanthanides and Actinides

- Cerium, samarium, terbium, dysprosium and ytterbium have three allotropes.
- Praseodymium, neodymium, gadolinium and terbium have two allotropes.
- Plutonium has six distinct solid allotropes under "normal" pressures. Their densities vary within a ratio of some 4:3, which vastly complicates all kinds of work with the metal (particularly casting, machining, and storage). A seventh plutonium allotrope exists at very high pressures. The transuranium metals Np, Am, and Cm are also allotropic.
- Promethium, americium, berkelium and californium have 3 allotropes each.

hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 ✱	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	mercury 79 Au 196.97	thallium 80 Hg 200.59	lead 81 Tl 204.38	bismuth 82 Pb 207.2	polonium 83 Bi 208.98	astatine 84 Po [209]	radon 85 At [210]	francium 86 Rn [222]					
francium 87 Fr [223]	radium 88 Ra [226]	89-102 ✱ ✱	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [269]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	unnilium 110 Uun [271]	ununium 111 Uuu [272]	unubium 112 Uub [277]	ununquadium 114 Uuq [289]										

* Lanthanide series

** Actinide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Glossary

ACTIVATED CARBON FILTRATION: Can remove organic chemicals that produce off-taste and odor. These compounds are not dangerous to health but can make the water unpleasant to drink. Carbon filtration comes in several forms, from small filters that attach to sink faucets to large tanks that contain removable cartridges. Activated carbon filters require regular maintenance or they can become a health hazard.

ADSORPTION: *Not to be confused with absorption.* Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins, and water purification.

Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms, and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding).

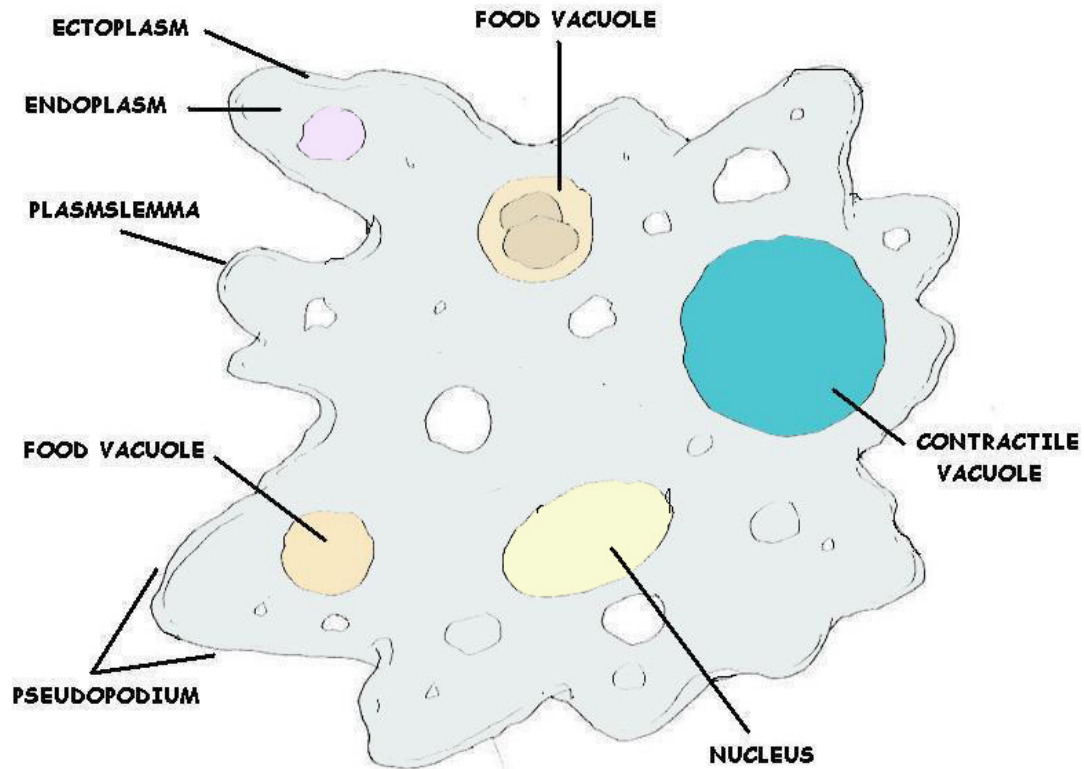
AIR GAP SEPARATION: A physical separation space that is present between the discharge vessel and the receiving vessel; for an example, a kitchen faucet .

ALTERNATIVE DISINFECTANTS: Disinfectants - other than chlorination (halogens) - used to treat water, e.g. ozone, ultraviolet radiation, chlorine dioxide, and chloramines. There is limited experience and scientific knowledge about the by-products and risks associated with the use of alternatives.

ALGAE: Microscopic plants that are free-living and usually live in water. They occur as single cells floating in water, or as multicellular plants like seaweed or strands of algae that attach to rocks.

ALPHA AND BETA RADIOACTIVITY: Represent two common forms of radioactive decay. Radioactive elements have atomic nuclei so heavy that the nucleus will break apart, or disintegrate spontaneously. When decay occurs, high-energy particles are released. These high-energy particles are called radioactivity. Although radioactivity from refined radioactive elements can be dangerous, it is rare to find dangerous levels of radioactivity in natural waters.

An alpha particle is a doubly-charged helium nucleus comprised of two protons, two neutrons, and no electrons. A beta particle is a high-speed electron. Alpha particles do not penetrate matter easily, and are stopped by a piece of paper. Beta particles are much more penetrating and can pass through a millimeter of lead.



AMOEBA

AMOEBA: Amoeba (sometimes amœba or ameba, plural amoebae) is a genus of protozoa that moves by means of pseudopods, and is well-known as a representative unicellular organism. The word amoeba or ameba is variously used to refer to it and its close relatives, now grouped as the Amoebozoa, or to all protozoa that move using pseudopods, otherwise termed amoeboids.

AMMONIA: A chemical made with Nitrogen and Hydrogen and used with chlorine to disinfect water.

APPROVAL AUTHORITY [40 CFR §403.3(c)]: The Director in an NPDES State with an approved State Pretreatment Program and the appropriate EPA Regional Administrator in a non-NPDES State or State without an approved pretreatment program.

APPROVED POTW PRETREATMENT PROGRAM[40 CFR §403.3(d)]: A program administered by a POTW that meets the criteria established in 40 CFR Part 403 and which has been approved by a Regional Administrator or State Director.

APPROVED STATE PRETREATMENT PROGRAM: A program administered by a State that meets the criteria established in 40 CFR §403.10 and which has been approved by a Regional Administrator

APPROVED /AUTHORIZED STATE: A State with an NPDES permit program approved pursuant to section 402(b) of the Act and an approved State Pretreatment Program.

AQUIFER: An underground geologic formation capable of storing significant amounts of water.

AS NITROGEN: An expression that tells how the concentration of a chemical is expressed mathematically. The chemical formula for the nitrate ion is NO_3 , with a mass of 62. The concentration of nitrate can be expressed either in terms of the nitrate ion or in terms of the principal element, nitrogen. The mass of the nitrogen atom is 14. The ratio of the nitrate ion mass to the nitrogen atom mass is 4.43. Thus a concentration of 10 mg/L nitrate expressed as nitrogen would be equivalent to a concentration of 44.3 mg/L nitrate expressed as nitrate ion. When dealing with nitrate numbers it is very important to know how numeric values are expressed.

A concentration of 22 mg/L nitrate expressed as nitrate ion sounds very high compared to a standard of 10 mg/L, but the standard is expressed as nitrogen. Converting 22 mg/L nitrate expressed as nitrate is only 4.9 mg/L nitrate expressed as nitrogen, less than half the drinking water standard. Older nitrate data (pre-1980) were commonly reported as nitrate, and that makes comparison with the drinking water standard difficult. For purposes of drinking water regulations, standards are expressed in the form of the principal element.

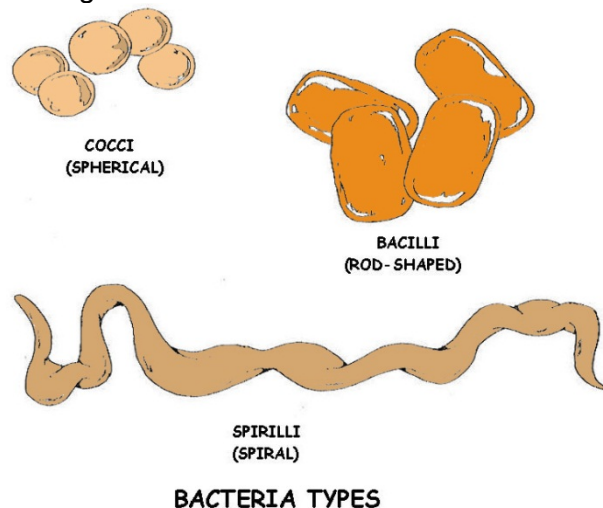
BACKFLOW: To reverse the natural and normal directional flow of a liquid, gas, or solid substance back into the public potable (drinking) water supply. This is normally an undesirable effect.

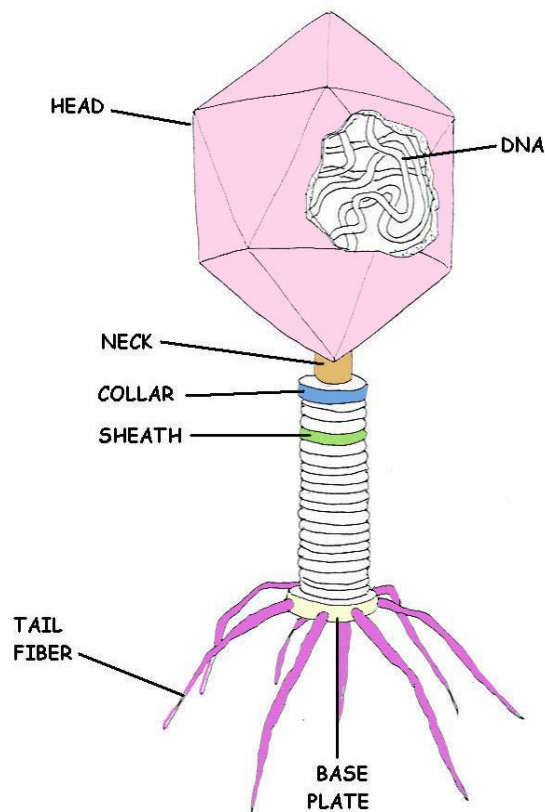
BACKFLOW PREVENTION: To stop or prevent the occurrence of, the unnatural act of reversing the normal direction of the flow of liquid, gases, or solid substances back in to the public potable (drinking) water supply. See Cross-connection control.

BACKSIPHONAGE: A liquid substance that is carried over a higher point. It is the method by which the liquid substance may be forced by excess pressure over or into a higher point.

BACTERIA: Small, one-celled animals too small to be seen by the naked eye. Bacteria are found everywhere, including on and in the human body. Humans would be unable to live without the bacteria that inhabit the intestines and assist in digesting food. Only a small percentage of bacteria cause disease in normal, healthy humans. Other bacteria can cause infections if they get into a cut or wound.

Bacteria are the principal concern in evaluating the microbiological quality of drinking water, because some of the bacteria-caused diseases that can be transmitted by drinking water are potentially life-threatening.





BACTERIOPHAGE

BACTERIOPHAGE: A bacteriophage (from 'bacteria' and Greek phagein, 'to eat') is any one of a number of viruses that infect bacteria. The term is commonly used in its shortened form, phage. Typically, bacteriophages consist of an outer protein hull enclosing genetic material. The genetic material can be ssRNA (single stranded RNA), dsRNA, ssDNA, or dsDNA between 5 and 500 kilo base pairs long with either circular or linear arrangement. Bacteriophages are much smaller than the bacteria they destroy - usually between 20 and 200 nm in size.

BASELINE MONITORING REPORT (BMR) [paraphrased from 40 CFR §403.12(b)]

A report submitted by categorical industrial users (CIUs) within 180 days after the effective date of an applicable categorical standard, or at least 90 days prior to commencement of discharge for new sources, which contains specific facility information, including flow and pollutant concentration data. For existing sources, the report must also certify as to the compliance status of the facility with respect to the categorical standards.

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE (BAT): A level of technology based on the best existing control and treatment measures that are economically achievable within the given industrial category or subcategory.

BEST MANAGEMENT PRACTICES (BMPs): Schedules of activities, prohibitions of practices, maintenance procedures, and other management practices to prevent or reduce the pollution of waters of the U.S. BMPs also include treatment requirements, operating procedures and practices to control plant site runoff, spillage or leaks, sludge or waste disposal, or drainage from raw material storage.

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE (BPT): A level of technology represented by the average of the best existing wastewater treatment performance levels within an industrial category or subcategory.

BEST PROFESSIONAL JUDGMENT (BPJ): The method used by a permit writer to develop technology-based limitations on a case-by-case basis using all reasonably available and relevant data.

BLOWDOWN: The discharge of water with high concentrations of accumulated solids from boilers to prevent plugging of the boiler tubes and/or steam lines. In cooling towers, blowdown is discharged to reduce the concentration of dissolved salts in the re-circulating cooling water.

BREAK POINT CHLORINATION: The process of chlorinating the water with significant quantities of chlorine to oxidize all contaminants and organic wastes and leave all remaining chlorine as free chlorine.

BROMINE: Chemical disinfectant (HALOGEN) that kills bacteria and algae.

BUFFER: Chemical that resists pH change, e.g. sodium bicarbonate

BYPASS [40 CFR §403.17(a)]: The intentional diversion of wastestreams from any portion of an Industrial User's treatment facility.

CALCIUM HARDNESS: A measure of the calcium salts dissolved in water.

CAUSTIC SODA: Also known as sodium hydroxide and is used to raise pH.

CATEGORICAL INDUSTRIAL USER (CIU): An industrial user subject to National categorical pretreatment standards.

CATEGORICAL PRETREATMENT STANDARDS [40 CFR § 403.6 and 40 CFR Parts 405-471] Limitations on pollutant discharges to POTWs promulgated by the EPA in accordance with Section 307 of the Clean Water Act, that apply to specific process wastewater discharges of particular industrial categories.

CHAIN OF CUSTODY (COC): A record of each person involved in the possession of a sample from the person who collects the sample to the person who analyzes the sample in the laboratory.

CHLORAMINES: A group of chlorine ammonia compounds formed when chlorine combines with organic wastes in the water. Chloramines are not effective as disinfectants and are responsible for eye and skin irritation as well as strong chlorine odors (also known as Combined Chlorine).

CHLORINE: A chemical used to disinfect water. Chlorine is extremely reactive, and when it comes in contact with microorganisms in water it kills them. Chlorine is added to swimming pools to keep the water safe for swimming. Chlorine is available as solid tablets for swimming pools. Some public water system's drinking water treatment plants use chlorine in a gas form because of the large volumes required. Chlorine is very effective against algae, bacteria and viruses. Protozoa are resistant to chlorine because they have thick coats; protozoa are removed from drinking water by filtration.

CHRONIC: A stimulus that lingers or continues for a relatively long period of time, often one-tenth of the life span or more. Chronic should be considered a relative term depending on the life span of an organism. The measurement of chronic effect can be reduced growth, reduced reproduction, etc., in addition to lethality.

COMBINED CHLORINE: The reaction product of chlorine with ammonia or other pollutants, also known as chloramines.

CONTAMINATE: tr.v. con·tam·i·nated, con·tam·i·nat·ing, con·tam·i·nates

1. To make impure or unclean by contact or mixture.

2. To expose to or permeate with radioactivity.

adj. Archaic (-nt)

CHLORINE DEMAND: Amount of chlorine required to react on various water impurities before a residual is obtained. Also, means the amount of chlorine required to produce a free chlorine residual of 0.1 mg/l after a contact time of fifteen minutes as measured by iodometric method of a sample at a temperature of twenty degrees in conformance with Standard methods.

CHLORINE, FREE: Chlorine available to kill bacteria or algae. The amount of chlorine available for sanitization after the chlorine demand has been met. Also known as chlorine residual.

CHLORAMINATION: Treating drinking water by applying chlorine before or after ammonia. This creates a persistent disinfectant residual.

CHLORINATION: The process in water treatment of adding chlorine (gas or solid hypochlorite) for purposes of disinfection.

CHLORINE: A chemical which destroys small organisms in water.

CLEAN WATER ACT (CWA): The common name for the Federal Water Pollution Control Act. Public law 92-500; 33 U.S.C. 1251 et seq.; legislation which provides statutory authority for both NPDES and Pretreatment Programs.

CODE OF FEDERAL REGULATIONS (CFR): A codification of Federal rules published annually by the Office of the Federal Register National Archives and Records Administration. Title 40 of the CFR contains the regulations for *Protection of the Environment*.

COMBINED SEWER OVERFLOW (CSO): A discharge of untreated wastewater from a combined sewer system at a point prior to the headworks of a publicly owned treatment works. CSOs generally occur during wet weather (rainfall or snowfall). During periods of wet weather, these systems become overloaded, bypass treatment works, and discharge directly to receiving waters.

COLIFORM: Bacteria normally found in the intestines of warm-blooded animals. Coliform bacteria are present in high numbers in animal feces. They are an indicator of potential contamination of water. Adequate and appropriate disinfection effectively destroys coliform bacteria.

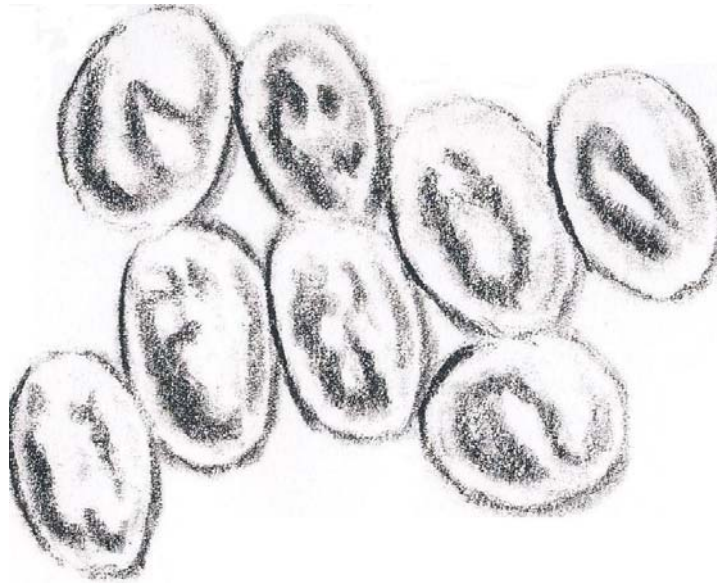
CONTAMINANT: Any natural or man-made physical, chemical, biological, or radiological substance or matter in water, which is at a level that may have an adverse effect on public health, and which is known or anticipated to occur in public water systems.

CONTAMINATION: To make something bad; to pollute or infect something. To reduce the quality of the potable (drinking) water and create an actual hazard to the water supply by poisoning or through spread of diseases.

CONVENTIONAL POLLUTANTS: BOD, TSS, fecal coliform, oil and grease, and pH.

CORROSION: The removal of metal from copper, other metal surfaces and concrete surfaces in a destructive manner. Corrosion is caused by improperly balanced water or excessive water velocity through piping or heat exchangers.

CROSS-CONTAMINATION: The mixing of two unlike qualities of water. For example, the mixing of good water with a polluting substance like a chemical.



CRYPTOSPORIDIUM: A disease-causing parasite, resistant to chlorine disinfection. It may be found in fecal matter or contaminated drinking water. Cryptosporidium is a protozoan pathogen of the Phylum Apicomplexa and causes a diarrheal illness called cryptosporidiosis. Other apicomplexan pathogens include the malaria parasite Plasmodium, and Toxoplasma, the causative agent of toxoplasmosis. Unlike Plasmodium, which transmits via a mosquito vector, Cryptosporidium does not utilize an insect vector and is capable of completing its life cycle within a single host, resulting in cyst stages which are excreted in feces and are capable of transmission to a new host.

CYANURIC ACID: Chemical used to prevent the decomposition of chlorine by ultraviolet (UV) light.

DESORPTION: Desorption is a phenomenon whereby a substance is released from or through a surface. The process is the opposite of sorption (that is, adsorption and absorption). This occurs in a system being in the state of sorption equilibrium between bulk phase (fluid, i.e. gas or liquid solution) and an adsorbing surface (solid or boundary separating two fluids). When the concentration (or pressure) of substance in the bulk phase is lowered, some of the sorbed substance changes to the bulk state. In chemistry, especially chromatography, desorption is the ability for a chemical to move with the mobile phase. The more a chemical desorbs, the less likely it will adsorb, thus instead of sticking to the stationary phase, the chemical moves up with the solvent front. In chemical separation processes, stripping is also referred to as desorption as one component of a liquid stream moves by mass transfer into a vapor phase through the liquid-vapor interface.

DETECTION LIMIT: The minimum concentration of an analyte(substance) that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero as determined by the procedure set forth in 40 CFR Part 136, Appendix B.

DISINFECT: The application of a chemical to kill most, but not all, microorganisms that may be present. Chlorine is added to public water drinking systems drinking water for disinfection. Depending on your state rule, drinking water must contain a minimum of 0.2 mg/L free chlorine. Disinfection makes drinking water safe to consume from the standpoint of killing pathogenic microorganisms including bacteria and viruses. Disinfection does not remove all bacteria from drinking water, but the bacteria that can survive disinfection with chlorine are not pathogenic bacteria that can cause disease in normal healthy humans.

DISINFECTION: The treatment of water to inactivate, destroy, and/or remove pathogenic bacteria, viruses, protozoa, and other parasites.

DISINFECTION BY-PRODUCTS (DBPs): The products created due to the reaction of chlorine with organic materials (e.g. leaves, soil) present in raw water during the water treatment process. The EPA has determined that these DBPs can cause cancer.

DRY ACID: A granular chemical used to lower pH and or total alkalinity.

EFFLUENT LIMITATIONS GUIDELINE: Any effluent limitations guidelines issued by EPA pursuant to Section 304(b) of the CWA. These regulations are published to adopt or revise a national standard prescribing restrictions on quantities, rates, and concentrations of chemical, physical, biological, and other constituents which are discharged from point sources, in specific industrial categories (e.g., metal finishing, metal molding and casting, etc).

ENFORCEMENT RESPONSE PLAN [paraphrased from 40 CFR §403.8(f)(5)]; Step-by-step enforcement procedures followed by Control Authority staff to identify, document, and respond to violations.

ENTAMOEBA HISTOLYTICA: Entamoeba histolytica, another water-borne pathogen, can cause diarrhea or a more serious invasive liver abscess. When in contact with human cells, these amoebae are cytotoxic. There is a rapid influx of calcium into the contacted cell, it quickly stops all membrane movement save for some surface blebbing. Internal organization is disrupted, organelles lyse, and the cell dies. The ameba may eat the dead cell or just absorb nutrients released from the cell.

EUGLENA: Euglena are common protists, of the class Euglenoidea of the phylum Euglenophyta. Currently, over 1000 species of Euglena have been described. Marin et al. (2003) revised the genus so and including several species without chloroplasts, formerly classified as *Astasia* and *Khawkinea*. Euglena sometimes can be considered to have both plant and animal features. *Euglena gracilis* has a long hair-like thing that stretches from its body. You need a very powerful microscope to see it. This is called a flagellum, and the euglena uses it to swim. It also has a red eyespot. *Euglena gracilis* uses its eyespot to locate light. Without light, it cannot use its chloroplasts to make itself food.

EXISTING SOURCE: Any source of discharge, the construction or operation of which commenced prior to the publication by the EPA of proposed categorical pretreatment standards, which will be applicable to such source if the standard is thereafter promulgated in accordance with Section 307 of the Act.

FEDERAL WATER POLLUTION CONTROL ACT (FWPCA): The title of Public law 92-500; 33 U.S.C. 1251 et seq., also known as the Clean Water Act (**CWA**), enacted October 18, 1972.

FILTRATION: The process of passing water through materials with very small holes to strain out particles. Most conventional water treatment plants used filters composed of gravel, sand, and anthracite. These materials settle into a compact mass that forms very small holes. Particles are filtered out as treated water passes through these holes. These holes are small enough to remove microorganisms including algae, bacteria, and protozoans, but not viruses. Viruses are eliminated from drinking water through the process of disinfection using chlorine.

GIARDIA LAMBLIA: *Giardia lamblia* (synonymous with *Lamblia intestinalis* and *Giardia duodenalis*) is a flagellated protozoan parasite that colonizes and reproduces in the small intestine, causing giardiasis. The giardia parasite attaches to the epithelium by a ventral adhesive disc, and reproduces via binary fission. Giardiasis does not spread via the bloodstream, nor does it spread to other parts of the gastro-intestinal tract, but remains confined to the lumen of the small intestine. *Giardia* trophozoites absorb their nutrients from the lumen of the small intestine, and are anaerobes.

GRAB SAMPLE: A sample which is taken from a water or wastestream on a one-time basis with no regard to the flow of the water or wastestream and without consideration of time. A single grab sample should be taken over a period of time not to exceed 15 minutes.

HALIDES: A halide is a binary compound, of which one part is a halogen atom and the other part is an element or radical that is less electronegative than the halogen, to make a fluoride, chloride, bromide, iodide, or astatide compound. Many salts are halides. All Group 1 metals form halides with the halogens and they are white solids. A halide ion is a halogen atom bearing a negative charge. The halide anions are fluoride (F), chloride (Cl), bromide (Br), iodide (I) and astatide (At). Such ions are present in all ionic halide salts.

HARDNESS: A measure of the amount of calcium and magnesium salts in water. More calcium and magnesium lead to greater hardness. The term "**hardness**" comes from the fact that it is hard to get soap suds from soap or detergents in hard water. This happens because calcium and magnesium react strongly with negatively-charged chemicals like soap to form insoluble compounds.

HETEROTROPHIC PLATE COUNT: A test performed on drinking water to determine the total number of all types of bacteria in the water.

HYDRIDES: Hydride is the name given to the negative ion of hydrogen, H. Although this ion does not exist except in extraordinary conditions, the term hydride is widely applied to describe compounds of hydrogen with other elements, particularly those of groups 1–16. The variety of compounds formed by hydrogen is vast, arguably greater than that of any other element. Various metal hydrides are currently being studied for use as a means of hydrogen storage in fuel cell-powered electric cars and batteries. They also have important uses in organic chemistry as powerful reducing agents, and many promising uses in hydrogen economy. Every element of the periodic table (except some noble gases) forms one or more hydrides. These compounds may be classified into three main types by the predominant nature of their bonding:

- * Saline hydrides, which have significant ionic character,
- * Covalent hydrides, which include the hydrocarbons and many other compounds, and
- * Interstitial hydrides, which may be described as having metallic bonding.

INORGANIC IONS: Present in all waters. Inorganic ions are essential for human health in small quantities, but in larger quantities they can cause unpleasant taste and odor or even illness. Most community water systems will commonly tests the concentrations of seven inorganic ions: nitrate, nitrite, fluoride, phosphate, sulfate, chloride, and bromide. Nitrate and nitrite can cause an illness in infants called methemoglobinemia. Fluoride is actually added to the drinking water in some public water systems to promote dental health. Phosphate, sulfate, chloride, and bromide have little direct effect on health, but high concentrations of inorganic ions can give water a salty or briny taste.

LOCAL LIMITS [paraphrased 40 CFR § 403.5(c)]: Specific discharge limits developed and enforced by POTWs upon industrial or commercial facilities to implement the general and specific discharge prohibitions listed in 40 CFR §§403.5(a)(1) and (b).

mg/L: Stands for "milligrams per liter." A common unit of chemical concentration. It expresses the mass of a chemical that is present in a given volume of water. A milligram (one one-thousandth of a gram) is equivalent to about 18 grains of table salt. A liter is equivalent to about one quart.

MICROORGANISMS: Are very small animals and plants that are too small to be seen by the naked eye and must be observed using a microscope. Microorganisms in water include algae, bacteria, viruses, and protozoa. Algae growing in surface waters can cause off-taste and odor by producing the chemicals MIB and geosmin. Certain types of bacteria, viruses, and protozoa can cause disease in humans. Bacteria are the most common microorganisms found in treated drinking water. The great majority of bacteria are not harmful. In fact, humans would not be able to live without the bacteria that inhabit the intestines. However, certain types of bacteria called coliform bacteria can signal the presence of possible drinking water contamination.

METALLOID: Metalloid is a term used in chemistry when classifying the chemical elements. On the basis of their general physical and chemical properties, nearly every element in the periodic table can be termed either a metal or a nonmetal. A few elements with intermediate properties are, however, referred to as metalloids. (In Greek metallon = metal and eidos = sort) There is no rigorous definition of the term, but the following properties are usually considered characteristic of metalloids:

- * metalloids often form amphoteric oxides.

* metalloids often behave as semiconductors (B,Si,Ge) to semimetals (e.g. Sb).

The concepts of metalloid and semiconductor should not be confused. Metalloid refers to the properties of certain elements in relation to the periodic table. Semiconductor refers to the physical properties of materials (including alloys, compounds) and there is only partial overlap between the two.

The following elements are generally considered metalloids:

- * Boron (B)
- * Silicon (Si)
- * Germanium (Ge)
- * Arsenic (As)
- * Antimony (Sb)
- * Tellurium (Te)

MILLILITER: One one-thousandth of a liter; A liter is a little more than a quart. A milliliter is about two drops from an eye dropper.

MONTHLY AVERAGE: The arithmetic average value of all samples taken in a calendar month for an individual pollutant parameter. The monthly average may be the average of all grab samples taken in a given calendar month, or the average of all composite samples taken in a given calendar month.

NONCONVENTIONAL POLLUTANTS: Any pollutant that is neither a toxic pollutant nor a conventional pollutant (e.g., manganese, ammonia, etc.)

NON-CONTACT COOLING WATER: Water used for cooling which does not come into direct contact with any raw material, intermediate product, waste product, or finished product. The only pollutant contributed from the discharge is heat.

NON-REGULATED WASTESTREAM: Unregulated and dilute wastestreams (not regulated by categorical standards).

OXIDE: An oxide is a chemical compound containing at least one oxygen atom as well as at least one other element. Most of the Earth's crust consists of oxides. Oxides result when elements are oxidized by oxygen in air. Combustion of hydrocarbons affords the two principal oxides of carbon, carbon monoxide and carbon dioxide. Even materials that are considered to be pure elements often contain a coating of oxides. For example, aluminum foil has a thin skin of Al_2O_3 that protects the foil from further corrosion. Virtually all elements burn in an atmosphere of oxygen. In the presence of water and oxygen (or simply air), some elements - lithium, sodium, potassium, rubidium, caesium, strontium and barium - react rapidly, even dangerously to give the hydroxides. In part for this reason, alkali and alkaline earth metals are not found in nature in their metallic, i.e., native, form. Caesium is so reactive with oxygen that it is used as a getter in vacuum tubes, and solutions of potassium and sodium, so called NaK are used to deoxygenate and dehydrate some organic solvents. The surface of most metals consists of oxides and hydroxides in the presence of air. A well known example is aluminum foil, which is coated with a thin film of aluminum oxide that passivates the metal, slowing further corrosion. The aluminum oxide layer can be built to greater thickness by the process of electrolytic anodizing. Although solid magnesium and aluminum react slowly with oxygen at STP, they, like most metals, will burn in air, generating very high temperatures. As a consequence, finely divided powders of most metals can be dangerously explosive in air.

OXIDIZED:

1. to convert (an element) into an oxide; combine with oxygen.
 2. to cover with a coating of oxide or rust.
 3. to take away hydrogen, as by the action of oxygen; add oxygen or any nonmetal.
 4. to remove electrons from (an atom or molecule), thereby increasing the valence. Compare REDUCE (def. 12).
- verb (used without object)
5. to become oxidized.
 6. (esp. of white wine) to lose freshness after prolonged exposure to air and often to darken in color.

PCE: abbr. perchloroethylene. Known also as perc or tetrachloroethylene, perchloroethylene is a clear, colorless liquid with a distinctive, somewhat ether-like odor. It is non flammable, having no measurable flashpoint or flammable limits in air. Effective over a wide range of applications, perchloroethylene is supported by closed loop transfer systems, stabilizers and employee exposure monitoring.

PERIODIC COMPLIANCE REPORT [*paraphrased from 40 CFR §403.12(e) & (h)*]: A report on compliance status submitted by categorical industrial users and significant non-categorical industrial users to the control authority at least semiannually (once every six months).

pH: A unit of measure which describes the degree of acidity or alkalinity of a solution. The pH scale runs from 0 to 14 with 7 being the mid point or neutral. A pH of less than 7 is on the acid side of the scale with 0 as the point of greatest acid activity. A pH of more than 7 is on the basic (alkaline) side of the scale with 14 as the point of greatest basic activity. The term pH is derived from "p", the mathematical symbol of the negative logarithm, and "H", the chemical symbol of Hydrogen. The definition of pH is the negative logarithm of the Hydrogen ion activity. $\text{pH} = -\log[\text{H}^+]$.

pH OF SATURATION: The ideal pH for perfect water balance in relation to a particular total alkalinity level and a particular calcium hardness level, at a particular temperature. The pH where the Langelier Index equals zero.

PHENOL RED: Chemical reagent used for testing pH in the range of 6.8 - 8.4.

POLLUTION: To make something unclean or impure. See Contaminated.

PATHOGENS: Disease-causing pathogens; waterborne pathogens A pathogen is a bacterium, virus or parasite that causes or is capable of causing disease. Pathogens may contaminate water and cause waterborne disease.

PICOCURIE: A unit of radioactivity. "Pico" is a metric prefix that means one one-millionth of one one-millionth. A picocurie is one one-millionth of one one-millionth of a Curie. A Curie is that quantity of any radioactive substance that undergoes 37 billion nuclear disintegrations per second. Thus a picocurie is that quantity of any radioactive substance that undergoes 0.037 nuclear disintegrations per second.

pCi/L: picocuries per liter A curie is the amount of radiation released by a set amount of a certain compound. A picocurie is one quadrillionth of a curie.

POLLUTANT [40 CFR 122.2]: Dredged spoil, solid waste, incinerator residue, filter backwash, sewage, garbage, sewage sludge, munitions, chemical wastes, biological materials, radioactive materials (except those regulated under the Atomic Energy Act of 1954, as amended (42 U.S.C. 2011 et seq.)), heat, wrecked or discarded equipment, rock, sand, cellar dirt, and industrial, municipal and agricultural waste discharged into water.

POTABLE: Good water which is safe for drinking or cooking purposes. **Non-Potable:** A liquid or water that is not approved for drinking.

PRETREATMENT STANDARDS FOR NEW SOURCES (PSNS): Categorical Standards and requirements applicable to industrial sources that began construction after the publication of the proposed pretreatment standards for that industrial category. (see individual standards at 40 CFR Parts 405-471.)

PRIORITY POLLUTANT: Pollutant listed by the Administrator of EPA under Clean Water Act section 307(a). The list of the current 126 Priority Pollutants can be found in 40 CFR Part 423 Appendix A.

PROCESS WASTEWATER: Any water which, during manufacturing or processing, comes into contact with or results from the production or use of any raw material, intermediate product, finished product, byproduct, or waste product.

PRODUCTION BASED STANDARDS: A discharge standard expressed in terms of pollutant mass allowed in a discharge per unit of product manufactured.

PROTOZOA: Microscopic animals that occur as single cells. Some protozoa can cause disease in humans. Protozoa form cysts, which are specialized cells like eggs that are very resistant to chlorine. Cysts can survive the disinfection process, then "hatch" into normal cells that can cause disease. Protozoa must be removed from drinking water by filtration, because they cannot be effectively killed by chlorine.

PUBLICLY OWNED TREATMENT WORKS (POTW) [40 CFR §403.3(o)]: A treatment works as defined by section 212 of the Act, which is owned by a State or municipality (as defined by section 502(4) of the Act). This definition includes any devices or systems used in the storage, treatment, recycling, and reclamation of municipal sewage or industrial wastes of a liquid nature. It also includes sewers, pipes or other conveyances only if they convey wastewater to a POTW Treatment Plant. The term also means the municipality as defined in section 502(4) of the Act, which has jurisdiction over the Indirect Discharges to and the discharges from such a treatment works.

REDOX POTENTIAL: Reduction potential (also known as redox potential, oxidation / reduction potential or ORP) is the tendency of a chemical species to acquire electrons and thereby be reduced. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species' affinity for electrons and tendency to be reduced. In aqueous solutions, the reduction potential is the tendency of the solution to either gain or lose electrons when it is subject to change by introduction of a new species. A solution with a higher (more positive) reduction potential than the new species will have a tendency to gain electrons from the new species (i.e. to be reduced by oxidizing the new species) and a solution with a lower (more negative) reduction potential will have a tendency to lose electrons to the new species (i.e. to be oxidized by reducing the new species). Just as the transfer of hydrogen ions between chemical species determines the pH of an aqueous solution, the transfer of electrons between chemical species determines the reduction potential of an aqueous solution. Like pH, the reduction

potential represents an intensity factor. It does not characterize the capacity of the system for oxidation or reduction, in much the same way that pH does not characterize the buffering capacity.

REGULATED WASTESTREAM: For purposes of applying the combined wastestream formula, a wastestream from an industrial process that is regulated by a categorical standard.

REMOVAL CREDIT [*paraphrased from 40 CFR §403.7*]: Variance from a pollutant limit specified in a categorical pretreatment standard to reflect removal by the POTW of said pollutant.

REPRESENTATIVE SAMPLE: A sample from a water or wastestream that is as nearly identical as possible in composition to that in the larger volume of water or wastewater being discharged and typical of the treatment process or the discharge from the facility on a normal operating day.

SANITARY SEWER OVERFLOW (SSO): Untreated or partially treated sewage overflows from a sanitary sewer collection system.

SELF-MONITORING: Sampling and analyses performed by a facility to ensure compliance with a permit or other regulatory requirements.

SEWER USE ORDINANCE (SUO): A legal mechanism implemented by a local government entity which sets out, among others, requirements for the discharge of pollutants into a publicly owned treatment works.

SODA ASH: Chemical used to raise pH and total alkalinity (sodium carbonate)

SODIUM BICARBONATE: Commonly used to increase alkalinity of water and stabilize pH.

SODIUM BISULFATE: Chemical used to lower pH and total alkalinity (dry acid).

SODIUM HYDROXIDE: Also known as caustic soda, A by-product chlorine generation and often used to raise pH.

SOLDER: A fusible alloy used to join metallic parts.

SULFIDE: The term sulfide refers to several types of chemical compounds containing sulfur in its lowest oxidation number of -2. Formally, "sulfide" is the dianion, S^{2-} , which exists in strongly alkaline aqueous solutions formed from H_2S or alkali metal salts such as Li_2S , Na_2S , and K_2S . Sulfide is exceptionally basic and, with a $pK_a > 14$, it does not exist in appreciable concentrations even in highly alkaline water, being undetectable at $pH < \sim 15$ (8 M NaOH). Instead, sulfide combines with electrons in hydrogen to form HS^- , which is variously called hydrogen sulfide ion, hydrosulfide ion, sulfhydryl ion, or bisulfide ion. At still lower pH's (< 7), HS^- converts to H_2S , hydrogen sulfide. Thus, the exact sulfur species obtained upon dissolving sulfide salts depends on the pH of the final solution. Aqueous solutions of transition metals cations react with sulfide sources (H_2S , $NaSH$, Na_2S) to precipitate solid sulfides. Such inorganic sulfides typically have very low solubility in water and many are related to minerals. One famous example is the bright yellow species CdS or "cadmium yellow". The black tarnish formed on sterling silver is Ag_2S . Such species are sometimes referred to as salts. In fact the bonding in transition metal sulfides is

highly covalent, which gives rise to their semiconductor properties, which in turn is related to the practical applications of many sulfide materials.

SURFACTANT: Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge).

TCE, trichloroethylene: A solvent and degreaser used for many purposes; for example dry cleaning, it is a common groundwater contaminant. Trichloroethylene is a colorless liquid which is used as a solvent for cleaning metal parts. Drinking or breathing high levels of trichloroethylene may cause nervous system effects, liver and lung damage, abnormal heartbeat, coma, and possibly death. Trichloroethylene has been found in at least 852 of the 1,430 National Priorities List sites identified by the Environmental Protection Agency (EPA).

TIME PROPORTIONAL COMPOSITE SAMPLE: A sample consisting of a series of aliquots collected from a representative point in the discharge stream at equal time intervals over the entire discharge period on the sampling day.

TITRATION: Method of testing by adding a reagent of known strength to a water sample until a specific color change indicates the completion of the reaction.

TOTAL ALKALINITY: A measure of the acid-neutralizing capacity of water which indicates its buffering ability, i.e. measure of its resistance to a change in pH. Generally, the higher the total alkalinity, the greater the resistance to pH change.

TOTAL DISSOLVED SOLIDS (TDS): The accumulated total of all solids that might be dissolved in water.

TREATED WATER: Disinfected and/or filtered water served to water system customers. It must meet or surpass all drinking water standards to be considered safe to drink.

TRIHALOMETHANES (THM): Four separate compounds including chloroform, dichlorobromomethane, dibromochloromethane, and bromoform. The most common class of disinfection by-products created when chemical disinfectants react with organic matter in water during the disinfection process. *See Disinfection Byproducts.*

TURBIDITY: A measure of the cloudiness of water caused by suspended particles.

RADIOCHEMICALS: Or radioactive chemicals, occur in natural waters. Naturally radioactive ores are particularly common in the Southwestern United States, and some streams and wells can have dangerously high levels of radioactivity. Total alpha and beta radioactivity and isotopes of radium and strontium are the major tests performed for radiochemicals. The federal drinking water standard for gross alpha radioactivity is set at 5 picocuries per liter.

REVERSE OSMOSIS: Forces water through membranes that contain holes so small that even salts cannot pass through. Reverse osmosis removes microorganisms, organic chemicals, and inorganic chemicals, producing very pure water. For some people, drinking highly purified water exclusively can upset the natural balance of salts in the body. Reverse osmosis units require regular maintenance or they can become a health hazard.

VIRUSES: Very small disease-causing microorganisms that are too small to be seen even with microscopes. Viruses cannot multiply or produce disease outside of a living cell.

VITRIFICATION: Vitrification is a process of converting a material into a glass-like amorphous solid that is free from any crystalline structure, either by the quick removal or addition of heat, or by mixing with an additive. Solidification of a vitreous solid occurs at the glass transition temperature (which is lower than melting temperature, T_m , due to supercooling). When the starting material is solid, vitrification usually involves heating the substances to very high temperatures. Many ceramics are produced in such a manner. Vitrification may also occur naturally when lightning strikes sand, where the extreme and immediate heat can create hollow, branching rootlike structures of glass, called fulgurite. When applied to whiteware ceramics, vitreous means the material has an extremely low permeability to liquids, often but not always water, when determined by a specified test regime. The microstructure of whiteware ceramics frequently contain both amorphous and crystalline phases.

VOLATILE ORGANIC COMPOUNDS: (VOCs) Solvents used as degreasers or cleaning agents. Improper disposal of VOCs can lead to contamination of natural waters. VOCs tend to evaporate very easily. This characteristic gives VOCs very distinct chemical odors like gasoline, kerosene, lighter fluid, or dry cleaning fluid. Some VOCs are suspected cancer-causing agents.

WATER QUALITY CRITERIA: Comprised of both numeric and narrative criteria. Numeric criteria are scientifically derived ambient concentrations developed by EPA or States for various pollutants of concern to protect human health and aquatic life. Narrative criteria are statements that describe the desired water quality goal.

WATER QUALITY STANDARD: A statute or regulation that consists of the beneficial designated use or uses of a waterbody, the numeric and narrative water quality criteria that are necessary to protect the use or uses of that particular waterbody, and an antidegradation statement.

WHOLE EFFLUENT TOXICITY: The total toxic effect of an effluent measured directly with a toxicity test.

Conversion Factors

1 PSI = 2.31 Feet of Water
1 Foot of Water = .433 PSI
1.13 Feet of Water = 1 Inch of Mercury
454 Grams = 1 Pound
1 Gallon of Water = 8.34 lbs/gallon
1 mg/L = 1 PPM
17.1 mg/L = 1 Grain/Gallon
1% = 10,000 mg/L
694 Gallons per Minute = MGD

LENGTH

12 Inches = 1 Foot
3 Feet = 1 Yard
5,280 Feet = 1 Mile

AREA

144 Square Inches = 1 Square Foot
43,560 Square Feet = 1 Acre

VOLUME

1000 Milliliters = 1 Liter

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