

THE REMOVAL OF ARSENIC FROM DRINKING WATER SUPPLIES



FOREWORD

Arsenic's evil reputation is manifested in its old alchemy symbol: a coiled serpent ready to strike. Considering arsenic's eminence as the preferred homicidal agent of detective novels, it is not surprising there is a great deal of anxiety over its possible presence in water, among other substances, we use on a daily basis.

With this bulletin, Pureflow© hopes to provide some facts on arsenic, its occurrence, normal routes of exposure, its health effects, and finally, the various unit operations available for its removal from water.

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*I am an evil, poisonous smoke...
But when from poison I am freed
Through art and sleight of hand,
Then can I cure both man and beast
From dire disease oft times direct them;
But prepare me correctly, and take great care
That you faithfully keep watch over me;
For else I am poison, and poison remain
That pierces the heart of many a one*

(Valentini 1694)

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OCCURRENCE AND USES OF ARSENIC

In the earth's crust, arsenic ranks as the twentieth most common element. In the human body it ranks twelfth (National Academy of Sciences). So, obviously, it is quite ubiquitous. Arsenic is present in all soils, ranging from 0.1 to 40 milligrams per kilogram (parts per million), and averaging between 1.5 - 2 milligrams per kilogram.

The arsenic content of a soil is a function of its geologic history. Sandstones, shales and coals associated with uranium mineralization in Utah, Colorado, Wyoming and South Dakota show higher than average arsenic content. This is also the case of phosphorites found in Florida, Montana and Idaho, as well as in British Columbia, Canada, southern Australia, the Far East, notably Taiwan, Africa, and parts of Europe.

Arsenic is found in at least 245 mineral species.

In base-metal mining and refining operations, arsenic, occurring along with lead, silver, zinc, copper and tin in their sulfide ores, is considered an expensive nuisance. Arsenic toxicity is also problematical near base-metal smelters. Regions of volcanic or geothermal activity usually show elevated arsenic concentrations.

Arsenic has had, and still has, many uses. In metallurgy the inclusion of 0.5 - 2% arsenic improves the sphericity of lead shot (McKee and Wolf). Inclusion of up to 5% arsenic in lead-based bearing alloys improves their high-temperature mechanical properties. Arsenic is added to other alloys to increase their hardness and heat resistance. High purity (99.999%) arsenic is used in semiconductor technology.

Arsenic is used in the manufacture of glass and ceramics.

Arsenic's major use has been, and remains, in farm chemicals. Approximately 97% of arsenic produced enters end-product manufacture in the form of "white arsenic," the remaining 3% as the metalloid for metallurgical purposes.

Agricultural uses accounted for about 81% of total arsenic consumption in the U.S. in 1973. Arsenic oxide is the raw material for arsenical pesticides. Compounds like paris green (copper acetoarsenite) used to be popular insecticides for orchard use but are of lesser importance today. Lead and calcium arsenate have also been used extensively in the U.S. for insect control on fruits, tobacco, cotton, and even some vegetables, but current use is slight.

Sodium arsenite came into use as an insecticide between 1920 and 1930, mainly as a bait and as livestock dip. Organic arsenicals are used extensively as selective herbicides for the post-emergence control of crabgrass, dalliograss, and other weedy grasses in turf. Disodium methanearsonate (DMSA) has been used extensively for cotton weed control. For example, in 1963, 71,000 acres in Mississippi were treated with DMSA as a directed spray, and more than 329,000 acres were treated in 1964.

Arsenic acid is used extensively as a cotton desiccant in Texas and Oklahoma to prepare cotton plants for mechanical stripping. It depletes the leaves and other plant tissues of moisture, thus facilitating harvesting. This is a more efficient method than mechanical harvesting. It is estimated that in Texas alone, over two million acres of cotton were treated with arsenic acid. Arsenic, along with copper, is used as a wood preservative in such things as telephone poles and pilings. There are additional uses for arsenic in human and veterinary pharmaceuticals.

EXPOSURE

The most significant and common route of exposure to arsenic is through food (Pontius, et al.). The average daily per capita intake of arsenic from food has been estimated at 50 micrograms, depending on geographical location and dietary habits. The daily per capita intake of arsenic from institutional food containing no seafood has been estimated at 400 μg (μg = microgram = 1 / 1000 mg) or 0.4 mg / day (Schroeder and Balassa). Saltwater fishes average about 10 milligrams of arsenic per kilogram of tissue or 10 parts per million (ppm), with mollusks and crustaceans at even higher levels (National Academy of Sciences). Four ounces (approximately 100 grams) of shrimp may contribute between 127 and 4,160 μg of arsenic, while the consumption of the same amount of tuna may add from 71 to 460 μg . Fresh water fishes, by comparison, average from 1-3 ppm.

The ingestion of arsenic from drinking water can also represent an important route of exposure. The United States Environmental Protection Agency (USEPA) bases most of its Maximum Contaminant Levels (MCL) on the ingestion of two liters of water per day per person. Water at the previous MCL for arsenic would thus have contributed 100 μg . (0.1 mg) of arsenic to the average individual each day. The newly adopted MCL reduces this daily intake to 20 μg (0.02 mg) per day.

Arsenic occurs in waters worldwide. About 3% of water analyses show arsenic to be present at concentrations greater than 50 μg / L (50 parts per billion). Thermal waters in Wyoming, California, Nevada, Alaska, and Iceland are reported to range from 20 - 3,800 μg / L, and water from the Waitapu Valley of New Zealand is said to contain up to 276,000 μg / L. As might be expected, arsenic levels are higher in well waters than in surface waters (National Academy of Sciences).

Well waters have been reported as ranging from "none detected" to 1,700 micrograms per liter (parts per billion, or 1.7 parts per million) and higher. Some well waters on Taiwan are reported to contain up to 1,800 μg / L and have been implicated in "Blackfoot Disease" and in skin cancers occurring in the southwest part of the island. In the Aomori Prefecture of Japan, groundwater is reported to contain arsenic up to 3,950 μg / L, while spring waters from the Kamchatka (former USSR) Peninsula are reported to contain approximately 1,000 μg / L (National Academy of Sciences). In one national survey, arsenic has been found in 39% of drinking water samples. For greater statistical occurrence detail for compliance with the variously suggested MCLs, please consult the American Water Works Association. It has been calculated, based on these national occurrence figures, that the average daily per capita contribution of arsenic from drinking water in the United States of America is about twenty micrograms.

Low levels of arsenic can be found in ambient air, probably as the result of the burning of fossil fuels, the smelting of ores, and other industrial uses (National Academy of Sciences). The Occupational Safety and Health Administration (OSHA) has recognized this and has set a Threshold Limit Value (TLV) for arsenic exposure from air at 500 micrograms per cubic meter, 200 micrograms per cubic meter for the (more toxic) arsine gas.

REGULATORY BACKGROUND

First regulated at 0.05 milligrams per liter (mg / L, parts per million) or 50 micrograms per liter (μg / L, parts per billion), by the United States Public Health Service (USPHS) in 1952, the National Interim Primary Drinking Water Regulations (NIPDWR) affirmed this concentration in 1975 as the Maximum Contaminant Level (MCL) [McKee and Wolf]. Since arsenic has been classified as a carcinogen (cancer-causing agent), the Maximum Contaminant Level Goal (MCLG) must, by law, be set at "zero" milligrams per liter.

The USEPA published the Final Arsenic Rule in January 2001, that reduced the maximum contaminant level from 50 μg / L to 10 μg / L (from 0.050 mg / L to 0.010 mg / L). The Final Arsenic Rule also mandated that the States must adopt the federal rule within two years of its promulgation, and set January 23, 2006, as the effective date of the new (10 μg / L) MCL. At that time all community and nontransient-noncommunity (NTNC) systems must begin monitoring or, when allowed by the State, submit data that meets grandfathering requirements.

The Final Rule also mandated that by July 1, 2002, and beyond, systems that detect arsenic above 10 μg / L must include a health effects statement in their Consumer Confidence Reports (CCR).

December 31, 2006, was the date for Surface Water Systems to have completed initial monitoring or have a state-approved waiver.

December 31, 2007, was the date for Ground Water Systems to have completed initial monitoring or have a state-approved waiver.

The Arsenic Rule provides that compliance calculations be based on a running annual average at each sampling point. Systems will not be in violation until one (1) year of quarterly samples have been collected (unless fewer samples would cause the running annual average to be exceeded). If a system fails to collect all required samples, compliance will be based on the running annual average of the samples collected.

HEALTH EFFECTS

At low doses, arsenic may be essential, or at least beneficial, for good health in humans, though no conclusive evidence to the element's essentiality has been documented.

Acute, high-dose, oral exposure to arsenic typically leads to gastrointestinal irritation, extreme thirst, hypotension (low blood pressure), and convulsions (National Academy of Sciences; Pontius, et al.). Death, when it occurs, is usually from cardiovascular collapse. The estimated lethal dose in adult humans is 70 - 180 milligrams, or between 1,000 to 2,600 micrograms of arsenic per kilogram of body weight.

While high-dose exposure is very unlikely, long-term exposure to 10 - 100 micrograms per kilogram per day commonly leads to neurological (nerve), dermatological (skin), or hepatic (liver) toxicity. Long-term exposures below 1 microgram / kg / day have not been observed to cause any detectable effects (National Academy of Sciences).

Evidence exists, however, that long-term exposure to arsenic increases cancer risk. When the exposure is by inhalation (as in some industrial exposures) the effect is an increased risk of lung cancer. When the exposure is by ingestion, the clearest effect is a greater risk of skin cancer, but there is evidence that the risk of internal cancer is also increased.

Arsenic exists in four valence (oxidation) states.

Valence is defined as the combining power of an element with other elements or compounds.



ARSENATE



ARSENITE



ELEMENTAL ARSENIC



ARSINE GAS

CHEMISTRY AND TOXICITY

In water, if arsenic is present, it is predominantly in the As^{+5} (arsenate) form. Arsenite (As^{+3}), when present, is readily oxidized to arsenate in aerobic waters at pH values above 7.0. Conversely, arsenate (As^{+5}) can be reduced to arsenite at low pH values.

Of the two predominant species, the trivalent form, arsenite (As^{+3}) is considerably more toxic than the pentavalent arsenate (As^{+5}) form, although it has been demonstrated that arsenate (As^{+5}) is better absorbed by the human body because it tends to react less with the membranes in the gastrointestinal tract (National Academy of Sciences).

Arsenic metabolism is a two-step process: arsenate (As^{+5}), entering a cell, is reduced to arsenite (As^{+3}), which is then methylated to methanearsonic acid ($\text{CH}_3\text{AsO}(\text{OH})_2$ (MMA) and / or dimethylarsinic acid ($\text{CH}_3)_2\text{AsO}(\text{OH})$ (DMA). Methylation is a detoxification step, since neither MMA nor DMA are as toxic to the system as is inorganic arsenic, although the chronic effects of MMA or DMA are not known (McKee and Wolf).

RAINWATER

0.02 - 16
 $\mu\text{g} / \text{L}$

RIVER
WATER

<0.02 - 21,800
 $\mu\text{g} / \text{L}$

LAKE WATER

<0.2 - 1,000
 $\mu\text{g} / \text{L}$

ESTUARINE
WATER

0.7 - 16 $\mu\text{g} / \text{L}$

SEAWATER

0.7 - 3.7 $\mu\text{g} / \text{L}$

OILFIELDS AND
RELATED BRINE

230 - 243,000
 $\mu\text{g} / \text{L}$

INDUSTRIAL
WATER FROM
MINE DRAINAGE

<1 - 850,000
 $\mu\text{g} / \text{L}$

GROUNDWATER

<0.5 - 50,000
 $\mu\text{g} / \text{L}$

ARSENIC REMOVAL PROCESSES

The USEPA has identified a number of treatment options for the removal of arsenic as Best Available Technology (BAT). Listed and discussed below, in no particular order of applicability, preference, efficiency or treatment cost, are some of the processes that are under consideration, or have been approved.

IRON BASED MEDIA

TITANIUM BASED MEDIA

ION EXCHANGE

COAGULATION-FILTRATION

REVERSE OSMOSIS

ACTIVATED ALUMINA

NANO-FILTRATION

LIME SOFTENING

COAGULATION ASSISTED MEMBRANE FILTRATION

ELECTRODIALYSIS

REVERSE OSMOSIS

This membrane process is primarily designed for the desalting of saline or brackish waters by the application of hydrostatic pressure (Montgomery). The process overcomes osmotic pressure and drives the water to be treated through a semi-permeable membrane designed to allow passage of water, but not of dissolved contaminants. The process requires expensive and fragile membrane stacks, either cellulose-acetate or thin film composite. Cellulose-acetate membranes can be operated at up to 400 psi, or more, but are subject to biological attack and hydrolysis. They also allow the salt passage to double after a service life of about 3 years. The more expensive thin film composite membranes are capable of the same, or greater, flux rate, but at half the applied pressure. These allow only a less than 30% increase in salt passage after 3 years. Both require considerable pre-treatment to prevent scaling, plugging, and colloidal or biological fouling of the membranes.

Since the recovery of product water, as a percentage of feed water, is a function of applied hydrostatic pressure (up to 400 psi, or more), the process tends to be quite energy intensive. Most reverse osmosis plants are designed for 75-80% recovery, i.e., up to 25% of the flow must be disposed of as a concentrated, possibly hazardous, waste (Montgomery). Reverse osmosis is quite capable of the removal of arsenic to very low levels. Process operation and maintenance costs, as well as labor intensity, will tend to rule out its application for all but small volume treatment systems.

NON REGENERABLE / DISPOSABLE MEDIA

IRON BASED MEDIA

ADSORBSIA™ / GTO™ is a disposable, white free-flowing, granular, adsorbent media. The granulation process produces a titanium oxide-based product that preserves the kinetic properties of its nanocrystalline structure in a physically stable media. Studies funded by the United States Department of Energy (USDOE) have demonstrated that ADSORBSIA™ / GTO™ media has kinetics approximately ten (10) times faster than those of currently available iron-based media. This kinetic advantage allows for flexible system design and faster flow rates. GTO™ media is NSF / ANSI 61 certified without limitations to flow or pre-treatment. GTO™ is effective in removing both As^{+3} and As^{+5} under all typical pH conditions. GTO™ media's capacity for arsenic removal is independent of sulfate, phosphate and vanadium concentrations, is very resistant to the presence of silica, and can be effectively used in existing system designs.

TITANIUM BASED MEDIA

Granular Ferric Hydroxide (GFH), and Granular Ferric Oxide (GFO) are iron based adsorptive media that are designed for the removal of arsenic and heavy metals, including phosphates, chromium, etc. Raw water pH and contaminant concentration (e.g., iron, manganese, chromium, organics, silica, phosphates, etc.) determine the life and effectiveness of the media, because they occupy the surface of the media designed to remove arsenic and, therefore, shorten the effective life of the media. Preoxidation of raw water is not required and both arsenic valence states are removed. Periodic backwashing of the media is required depending on raw water quality. These media are presently classified as non-regenerative media that, when exhausted, must be removed from the filter vessel, and replaced with new media. Research is being conducted to determine the feasibility of regenerating GFH. Spent media is hauled to a landfill for disposal. Toxicity Characteristic Leaching Procedure (TCLP) testing is a federal test commonly used to determine if the spent media is classified as hazardous or non-hazardous. State regulations should be consulted to verify acceptable testing methods and media disposal requirements.

ION EXCHANGE

Capable of complete removal of all dissolved matter, including arsenic, chromium and uranium, from water, this process is used for the production of de-ionized and potable water. The resin does not require pH adjustment or raw water pre-oxidation. Recent advances in resin technology have replaced the weak-base anion resins with strong-base anion resins. Pentavalent arsenic (As^{+5}), being present as the divalent anion $HASO_4^{-2}$, appears to have a greater affinity for this type of resin. Strong base resins permit the use of ordinary sodium chloride brine for regeneration and eliminate the need for the use of strong acids. Typically, columns are rinsed with 1-2 bed volumes to displace the regenerant. This is followed by a fast rinse for about 10 minutes at design flow. The used regeneration brine, containing arsenic, can be a hazardous waste and must be disposed of accordingly. Raw water contaminants such as iron, manganese, sulfides, etc. can cause fouling of the resin requiring more frequent regeneration and / or resin replacement long before its expected life cycle. Fouling will also shorten the expected life cycle of non-regenerable media.

ACTIVATED ALUMINA

Activated alumina has a long history of use as an adsorptive treatment technology for arsenic removal. The media is a byproduct of aluminum production. It is primarily an aluminum oxide that has been activated by exposure to high temperature and caustic soda.

The material is extremely porous and has a high average surface area per unit weight ($350\text{m}^2/\text{g}$). The capacity for arsenic removal by activated alumina is pH-dependent, with the maximum removal capacity achieved at pH 5.5. Adjusting the pH of the source water, therefore, provides removal capacity advantages. As the pH deviates from the 5.0 - 6.0 range, the adsorption capacity for arsenic decreases at an increasing rate. Process demonstrations have shown that arsenic removal capacity has been reduced by more than 15% at pH 6.0 compared to that of pH 5.5 (Rubel, 1984).

Fluoride, selenium, and other inorganic ions and organic molecules are also removed by the same pH-adjusted activated alumina process. The process, however, is preferential for arsenic at the optimum pH level of 5.5. Other ions that compete with arsenic for the same adsorptive sites at other pH levels are not adsorbed in the pH range of 5.0 - 6.0. Included are silica and hardness ions that are adsorbed in the pH range of 7 - 10.

Activated alumina can either be regenerated or replaced with new media when the selected breakthrough point is reached. At the optimum pH for arsenic removal, fluoride, selenium, some organic molecules, and some trace heavy metal ions are adsorbed; however, these are also completely removed during regeneration, along with arsenic. Because these ions use the same adsorptive sites as arsenic, their presence will deplete the alumina capacity for arsenic. When excess fluoride and arsenic are present in the water supply, a special treatment technique is required (Rubel and Williams, 1980).

The capacity of many adsorptive media, particularly activated alumina, is pH sensitive; removal capacity increases with decreasing pH. Employing pH adjustment, therefore, generally provides cost advantages regardless of whether the media is regenerated or replaced. Because the pH adjustment chemicals are usually the same chemicals that are used for regeneration, it is generally advantageous to couple regeneration with pH adjustment systems when the media can be regenerated (Rubel 2003).

LIME SOFTENING

Excess lime softening is the addition of a sufficiently high lime dosage, at times in excess of 1 gram per liter, to obtain a pH greater than 11.5. It has long been used for the removal of calcium and magnesium carbonate hardness and is also capable of the removal of approximately 90% of any arsenic that may be present (Dutta and Chauderi).

The removal of trivalent arsenic appears to be dependent upon the precipitation of magnesium hydroxide, $\text{Mg}(\text{OH})_2$. The addition of powdered activated carbon, though apparently not absolutely necessary, appears to enhance removal efficiency. While this is an old, tried and true process, and while, apparently, quite capable of arsenic removal, the process remains plant and chemical intensive, requires the re-carbonation of the water, and produces large volumes of sludge. For these reasons, unless there is also a demonstrated need for softening, the process may not be deemed economically viable.

COAGULATION-FILTRATION

Conventional coagulation / flocculation / filtration, using iron salts to co-precipitate arsenic, is effective in the removal of arsenate (As^{+5}), usually at pH levels of 7 or less (Edwards), to near non- detectable levels. Above a pH of 7, flocs from iron salts are usually less effective in removing arsenic, with some exceptions, depending on raw water quality. Iron coagulants will remove about 50% of trivalent arsenic (As^{+3}) (Montgomery), thus, it is very important to fully oxidize As^{+3} to As^{+5} , with chlorine, or another strong oxidant, prior to coagulation to achieve greatest removal.

High arsenic concentrations are frequently found in anaerobic waters. These same waters are generally high in ferrous iron (Fe^{+2}), and / or manganous manganese (Mn^{+2}), necessitating their removal. Iron / manganese removal processes relying on the oxidation, and subsequent precipitation of the metals as hydroxides, will also effectively remove soluble arsenic by co-precipitation and / or adsorption reactions. It is almost as though the presence of the iron and manganese to be removed is analogous to a natural coagulant addition, as it facilitates the removal of arsenic. Removals of soluble arsenate (As^{+5}) during ferrous iron oxidation and precipitation processes are very significant. This is likely not the case during soluble manganese (Mn^{+2}) oxidation alone. In such cases, the addition of iron salts ahead of the filter is indicated.

Of the arsenic removal processes available and discussed in this bulletin, iron coagulation, whether practiced primarily for the removal of arsenic, or also of iron / manganese, appears to be the most promising, cost effective, and proven process available. This process is capable of the removal of 90%, or more, of any arsenic present, and in many systems the arsenic removal is at, or near, non-detectable levels. Furthermore, many such systems are already in existence and operating efficiently, albeit they were initially designed for the removal of iron and manganese only.

COAGULATION – FILTRATION MEDIA

Various media can be used in the coagulation - filtration process to remove arsenic from potable water. Typical media used for this application include silica sand, garnet sand, manganese greensand, anthrasand, proprietary adsorptive types, and manganese dioxide (pyrolusite) media. The effectiveness of each of these media is site specific and is dependent on raw water quality, pretreatment chemical feed and regeneration (when required). A field pilot study is, therefore, essential in order to determine which media is most effective in treating a particular drinking water supply. The criteria for determining the effectiveness of a media should include the removal of arsenic and other contaminants, initial capital cost, operation and maintenance costs (including regeneration and media replacement, if required), and twenty (20) year life cycle costs.

SILICA SAND / GARNET SAND AND ANTHRACITE

Standard silica sand (or garnet sand) and anthracite media have been used to remove arsenic / iron / manganese from drinking water supplies since the earliest days of water treatment. Aeration, followed by storage, to give the arsenic / iron / manganese time to oxidize / flocculate, preceded slow sand filters that rely on the iron / manganese in the raw water to naturally coat the media in the filter vessel. Coating the media with iron / manganese aids in the removal of these metals as well as the arsenic.

Current silica sand / garnet sand (and anthracite) filter designs include pretreatment with chlorine to oxidize the arsenic / iron / manganese (and other contaminants, such as hydrogen sulfide, organics, etc.), and also an iron salt feed (e.g., ferric chloride $[\text{FeCl}_3]$). This process eliminates aeration / storage, and relies on the chlorine to oxidize contaminants, and the iron salt to co-precipitate the arsenic and provide the required iron coating on the sand. The time required to condition the silica sand, or garnet sand, with a complete coating of iron / manganese is site specific, depending on raw water quality. It can take days, weeks or months, in some cases, to complete the sand coating process required to achieve an effluent water quality that meets USEPA / USDHS standards. Typical flux rates (gpm / ft^2 of media) are considerably less than catalytic type media.

ANTHRASAND

Anthrasand is a filter media that is similar to greensand and Greensand Plus. A base material of standard silica sand (or garnet sand) is capped with anthracite in a conventional dual media configuration. The sand and anthracite are placed in the filter vessel where they are soaked in a manganous salt solution for a prescribed period of time. Potassium permanganate (KMnO_4) is then added to oxidize the manganous ion to the MnO_2 form(s). This process applies a thin layer of MnO_2 on the media and is referred to as in-situ generated manganese dioxide (MnO_2).

The suggested pretreatment for the operation of an anthrasand filtration process includes dosing the raw water (ahead of the filter) with KMnO_4 to oxidize the arsenic / iron / manganese. Sufficient (excess) KMnO_4 is fed to maintain the MnO_2 coating on the silica (or garnet) sand in a regenerated condition. Chlorine can also be fed as a pretreatment chemical to oxidize other contaminants, as well as the arsenic / iron / manganese, and to provide a disinfection residual. Feeding chlorine does not eliminate the requirement to feed potassium permanganate. If sufficient iron (Fe) is not present in the raw water an iron salt (e.g., ferric chloride $[\text{FeCl}_3]$) is fed to co-precipitate the arsenic.

Establishing, and maintaining, a complete and fully oxidized MnO_2 coating in-situ can be difficult, depending on the raw water chemistry. Silica / garnet sand does not generally have the same ion exchange properties as the glauconite sand that is used to process manganese greensand, nor does it have surface areas increased by pockets, or caves, as is the case with glauconite sand.



MANGANESE GREENSAND

Manganese greensand / greensand is manufactured by coating various minerals (glauconite, silica sand etc.) with manganese dioxide. These media operate on the chemical principles of oxidation and reduction, and the catalytic effect of the manganese oxide coating. Pretreatment chemical oxidation is required. The most common chemicals used are potassium permanganate (KMnO_4), and chlorine (Cl_2), or a combination of the two (2), fed in series.

Regeneration of the manganese oxide coating is required to extend the life cycle of the media, and is accomplished by two (2) distinct methods of operation; either Continuous Regeneration (CR) or Intermittent Regeneration (IR) depending upon raw water characteristics. The CR method uses a continuous feed of potassium permanganate, or a combination of chlorine and KMnO_4 at stoichiometric dosage rates. The IR method uses KMnO_4 (at a higher dosage rate) to regenerate the media during each backwash cycle.

Greensand media will remove arsenic, iron and manganese without regeneration, however, if it is not regenerated, the manganese oxide coating will either wear off, or may become permanently fouled (with iron or manganese) which will result in media blinding. The greensand media will gradually lose its effectiveness and may require replacement before the end of its expected life cycle. If sufficient iron (Fe) is not present in the raw water an iron salt (e.g., ferric chloride [FeCl_3]) is fed to co-precipitate the arsenic.

GREENSAND PLUS

Greensand Plus is a filter media that is similar to manganese greensand. The difference between manganese greensand and Greensand Plus is in the substrate that forms the core of the media, and the method by which the manganese dioxide (MnO_2) coating is attached to that substrate. The substrate of manganese greensand is glauconite sand, and the substrate of Greensand Plus is silica sand. The manganese dioxide coating is ionically bound to the manganese greensand, while the manganese dioxide coating is fused to the silica sand core of Greensand Plus. Regeneration of the manganese dioxide coating on Greensand Plus is recommended to extend the life cycle of the media, and is accomplished by either feeding potassium permanganate (KMnO_4) continuously, at relatively low dosage rates, (CR) or intermittently at higher dosage rates (IR). Chlorine can be fed ahead of the Greensand Plus to oxidize contaminants but will not regenerate the media. If sufficient iron is not present in the raw water an iron salt is fed to co-precipitate the arsenic. Greensand Plus is an exact replacement for manganese greensand and requires no changes in backwash rate, duration, or chemical feed.

MANGANESE DIOXIDE

Manganese dioxide (MnO_2) is a natural manganese ore that is selected for its capacity to attract heavy metals, such as iron / manganese, and for the co-precipitation of arsenic, along with other contaminants, such as hydrogen sulfide (H_2S). Manganese dioxide media does not affect the alkalinity, or the pH, of the filtered water, does not add any extraneous species during treatment, and is not a coated media.

Sometimes referred to as pyrolusite, manganese dioxide is a catalytic adsorptive media that can operate at high flux and loading rates, depending on the raw water contaminant levels, and the reactivity of the manganese dioxide media. Contaminants in the raw water (arsenic, iron, manganese, hydrogen sulfide, etc.) are first oxidized (usually with chlorine) and are then adsorbed onto the filter media. Manganese dioxide is a permanent media that is backwashed with filtered water, and does not require chemical regeneration.

Some proprietary blends of high - manganese content manganese dioxide have elevated catalytic activity. The increased catalytic activity results in the removal of contaminants such as arsenic, iron, manganese, sulfides, etc. without pretreatment chemical oxidation. This is because the manganese dioxide media acts as an oxidizing agent, and oxidizes As, Fe, Mn, H_2S etc., and then adsorbs these contaminants. (e.g., H_2S is oxidized to elemental sulfur which deposits onto the surface of the manganese dioxide). These media also do not affect the alkalinity of the water, and can be used as a disposable media. When used without a pretreatment chemical oxidant this media can also be regenerated periodically with sodium hypochlorite, if manganese is being removed, or, in the case of arsenic removal, the adsorbed arsenic may be removed with a dilute solution of sodium hydroxide or nitric acid, followed by thorough backwashing, thus extending the "life cycle" of the media.

CATALYTIC ADSORPTIVE MEDIA

Catalytic adsorptive media provide a strong attraction to heavy metals, such as iron / manganese. These, sometimes proprietary, media have the ability to operate at relatively high flux rates (10-15 gpm / ft^2 for the removal of Fe / Mn), and high loading rates. In addition, catalytic adsorptive media have a low backwash to filtration ratio (approximately 1 - 3% of produced water). Filtered water is used to backwash the media at 20 gpm / ft^2 of media, for four (4) minutes, with a one (1) minute purge.

Chemical pretreatment with a strong oxidant (chlorine, ozone, etc.) is required to oxidize the heavy metals / arsenic, and other dissolved contaminants, such as organic carbons, hydrogen sulfide, etc. Detention time is not required to oxidize these contaminants, rather, an inline static mixer is suggested. Iron / manganese are precipitated as hydroxides, arsenic co-precipitates with the iron. These are permanent media that do not require chemical regeneration. If sufficient iron (Fe) is not present in the raw water, an iron salt is fed to co-precipitate the arsenic. Typical flux rates (gpm / ft^2 of media) for arsenic removal are lower (approximately 7.5 gpm / ft^2) than the 10-15 gpm / ft^2 used for iron / manganese removal.

ELECTRODIALYSIS (ED) AND ELECTRODIALYSIS REVERSAL (EDR)

ED is an electrochemical membrane process initially developed for the treatment of saline or brackish waters (Montgomery). Instead of hydrostatic pressure, the process uses an applied direct current (DC) voltage to move dissolved anions and cations from alternate cells through semi-permeable membranes. This purifies a portion of the feed water, while concentrating another. While capable of removing arsenic to low levels, the process is equipment, energy and labor intensive. It also creates a concentrate which must be disposed of properly, and is usually a significant percentage of the treated water.

EDR is an ED process which reverses the polarity of the electrodes on a controlled time cycle, which in turn reverses the direction of ion movement in a membrane stack. Reversing polarity provides automatic flushing of scale forming minerals from the surface of the membrane. EDR typically requires little or no pretreatment to minimize fouling of the membrane. ED / EDR systems are not considered to be economically viable for any but very small installations.

NANO-FILTRATION

This process, also known as “membrane softening” uses an ultra-low-pressure membrane designed to allow only passage of particles less than 1 nanometer (10 Angstroms) in size. It is, thus, very efficient (more so than Reverse Osmosis) in the removal of dissolved matter, but is, of course, not selective for arsenic only. Like all other membrane processes, extensive pretreatment is necessary to prevent fouling of the delicate and expensive membranes caused by particulate matter, scaling, or biofouling.

COAGULATION ASSISTED MEMBRANE PROCESS (CAMP)

Coagulation Assisted Membrane Process (CAMP) is considered to be a promising technology for arsenic removal because it can be applied over a wide range of water quality. Water that contains high turbidity, iron, manganese, sulfates and nitrates can also be treated with CAMP. Low pressure membranes (e.g., microfiltration and ultrafiltration) are very effective in removing particulate arsenic, but without a pre-coagulation step, low pressure membranes are ineffective at removing soluble arsenic.

Metal based coagulants, such as ferric chloride, can be used to bind the arsenic which is removed with the ferric floc on the membrane. The use of low-pressure membranes eliminates the breakthrough of arsenic-laden coagulant flocs (a typical occurrence with conventional granular media filters) by taking advantage of the membranes’ particle barrier. Factors affecting the CAMP process include ferric chloride dosage, pH, mixing and floc formation (contact time).

As with all membrane processes, provision for adequate pretreatment to control feed water quality should be taken to protect the membrane from fouling caused by particulate matter, scaling and / or biofouling to optimize membrane performance and life. Disposal of the reject coagulant (which is not considered to be a hazardous waste) can be to a sanitary sewer.

PILOT TESTING

Since varying ground water quality can significantly affect arsenic removal processes, pilot testing at each well site is strongly recommended. Raw water quality analyses should be made prior to pilot testing to determine all of the constituents in the water that can affect arsenic removal processes.

The pilot filter system should be designed to treat all of the constituents in the raw water that will affect the efficiency of the treatment process. On-site testing should be verified by raw and treated water samples that are tested by at least two (2) independent, certified laboratories.

The pilot process should include pretreatment equipment, as dictated by the raw water quality analysis, to assure continued treatment to below USEPA standards and to maximize process runs and optimize media / membrane life. The pilot system must verify removal of arsenic throughout the process run cycle as well as determine pretreatment chemical requirements, and, in addition, the following costs: operations, labor, media disposal and replacement, membrane disposal and replacement, and / or regenerant brine disposal.

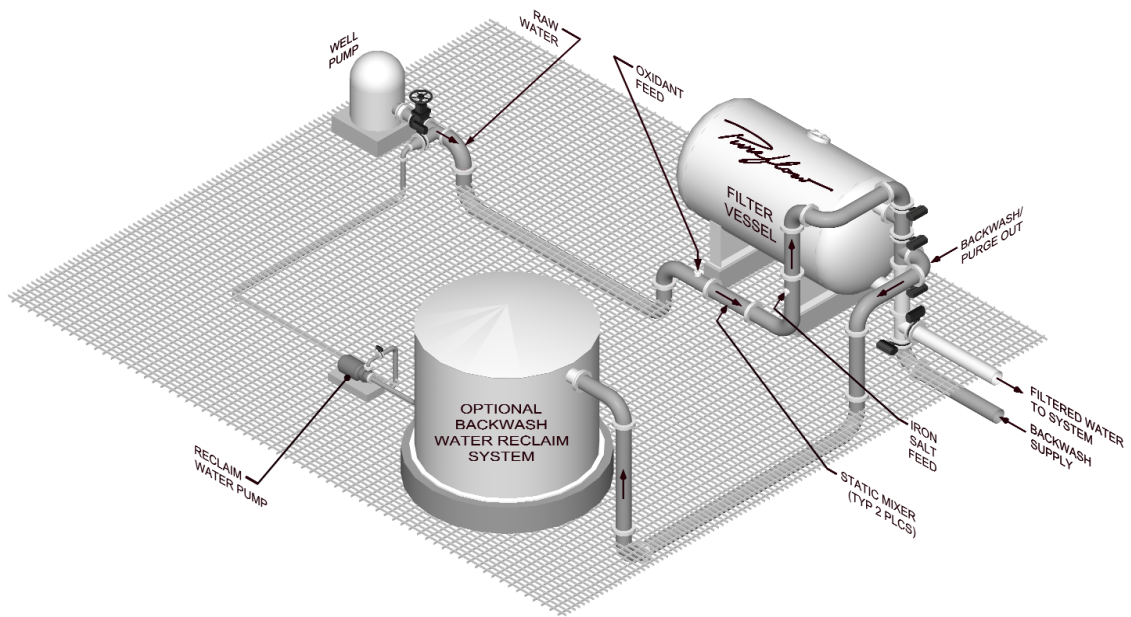
CONCLUSION

Arsenic, long known as the poison of choice because of its legendary toxicity at high doses, has been implicated in skin and internal carcinogenesis, thus the requirement for regulation at the current USEPA level of 0.010 mg / L or 10.0 µg / L.

The current MCL will largely drive and dictate the installation of arsenic removal processes. Of the removal processes available, iron and arsenic oxidation, followed by coagulation - filtration, appears to be the most promising, especially for those raw water sources with contaminants that will reduce the effective life of disposable media. Meanwhile, many researchers are exploring modifications to conventional treatment, with a particular emphasis on enhancing existing coagulation - filtration operations.

Pilot testing should be conducted at each well site to verify arsenic removal rates, process design and operational costs.

***COAGULATION - FILTRATION PROCESS FOR ARSENIC REMOVAL**



TYPICAL INSTALLATION

***Refer to pages 10, 11 and 12 for a description of the coagulation - filtration process for arsenic removal**

REFERENCES

AWWA Final Report, National Drinking Water Advisory Council (2001)

AWWA Water Quality and Treatment (4th Edition) - AWWA Journal April 2008

AWWA Iron and Manganese Removal Handbook, 1999

Dutta, A. and Chauduri, M. "Removal of Arsenic From Groundwater by Lime Softening with Powdered Coal Additive." JWater, SRT-Aqua 40.1 (1991)

Edwards, M. "Chemistry of Arsenic Removal During Coagulation and Iron and Manganese Oxidation." JAWWA 86.9 (1994)

"Feasibility Studies of Using Coagulation Assisted Membrane Processes For Arsenic Removal." HDR Engineering, Bellevue, WA (2001)

Marquez et al, 2005 (AWWA Journal April 2008)

McKee and Wolf. Water Quality Criteria. Water Quality Control Board, State of CA (1963)

Montgomery, J.M., Consulting Engineers. Water Treatment Principles and Design. Wiley Interscience Publications. (1985)

National Academy of Sciences. Drinking Water and Health. Vol. III National Academy Press, Washington, D.C. (1980)

Pontius, F.W. Safe Drinking Water Act Advisor. American Water Works Association. (1994)

Pontius, F.W., et al. "Health Implications of Arsenic in Drinking Water." JAWWA 86.9 (1994)

Rubel, Frederick Jr. P.E., "Design Manual: Removal of Arsenic from Drinking Water by Adsorptive Media". (March 2003)

Schroeder and Balassas. Journal of Chronic Diseases. 19:85-106 (1966)

Smedley and Kinniburgh, 2002 (AWWA Journal April 2008)

Stewart, H.T. and Kessler, K.J. "Evaluation of Arsenic Removal by Activated Alumina Filtration at a Small Community Public Water System." Journal NEWWA (Sept 1991)

United States Environmental Protection Agency (USEPA), Final Arsenic Rule, (January 20, 2001)

United States Environmental Protection Agency (USEPA). Toxicity Characteristic Leaching Procedure (TCLP test). Test methods that are used to characterize waste products as hazardous or non-hazardous for the purpose of waste disposal.

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