
2 Toxicity and Sources of Pb, Cd, Hg, Cr, As, and Radionuclides in the Environment

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2.1 METAL TOXICITY

Out of 106 identified elements, about 80 of them are called metals. These metallic elements can be divided into two groups: those that are essential for survival, such as iron and calcium, and those that are nonessential or toxic, such as cadmium and lead. These toxic metals, unlike some organic substances, are not metabolically degradable and their accumulation in living tissues can cause death or serious health threats. Furthermore, these metals, dissolved in wastewaters and discharged into surface waters, will be concentrated as they travel up the food chain. Eventually, extremely poisonous levels of toxin can migrate to the immediate environment of the public. Metals that seep into groundwaters will contaminate drinking water wells and harm the consumers of that water.

Pollution from man-made sources can easily create local conditions of elevated metal presence, which could lead to disastrous effects on animals and humans. Actually, man's exploitation of the world's mineral resources and his technological activities tend to unearth, dislodge, and disperse chemicals and particularly metallic elements, which have recently been brought into the environment in unprecedented quantities and concentrations and at extreme rates. Man's new technologies involving nuclear fission opened up a whole new area of hope and concern at the same time. Radioactive isotopes of elements and, indeed, new elements have been discovered and handled in historically unprecedented quantities and concentrations. The sneaking and deadly danger of radioactivity associated particularly with long-lived and high-radiation isotopes has cast a shadow over our lives. Actually, the disposal problems concerning radioactive isotopes originating directly or indirectly from the operation of nuclear generating facilities have produced a considerable slow-down in deployment of this technology, which, after all, may only be a transient phase made obsolete by the dangers it generates.

2.1.1 SELECTED HEAVY METALS

Heavy metals can be defined in several ways. One possible definition is the following: Heavy metals form positive ions in solution and they have a density five times greater than that of water. They are of particular toxicological importance. Many metallic elements play an essential role in the function of living organisms; they constitute a nutritional requirement and fulfill a physiological role. However, overabundance of the essential trace elements and particularly their substitution by non-essential ones, such as the case may be for cadmium, nickel, or silver, can cause toxicity symptoms or death. Humans receive their allocation of trace elements from food and water, an indispensable link in the food chain being plant life, which also supports animal life. It is a well-established fact that assimilation of metals takes place in the microbial world as well as in plants, and these elements tend to get concentrated as they progress through the food chain. It has been shown that spectacular metal enrichment coefficients of the order of 10^5 – 10^7 can occur in cells [1]. Imbalances or excessive amounts of a metal species along this route lead to toxicity symptoms, disorders in the cellular functions, long-term debilitating disabilities in humans, and eventually death.

2.1.1.1 Lead

Lead is the most common of the heavy elements. Several stable isotopes exist in nature, ^{208}Pb being the most abundant. The average molecular weight of lead is 207.2. Lead is a soft metal that resists

corrosion and has a low melting point (327°C). From a drinking water perspective, the almost universal use of lead compounds in plumbing fittings and as a solder in water distribution systems is important. Distribution systems and plumbing installed before 1945 were made from lead pipes [2]. Solid and liquid (sludge) wastes account for more than 50% of the lead discharged into the environment, usually into landfills, but lead has been dispersed more widely in the general environment through atmospheric emissions—particularly from car exhausts. With the introduction of unleaded fuel, lead emissions from this source declined. The annual consumption of lead is in the order of 3 million tons, of which 40% is used in the production of electrical accumulators and batteries, 20% is used in gasoline as alkyl additives, 12% in building construction, 6% in cable coatings, 5% in ammunition, and 17% in other usages. It is estimated that approximately 2 million tons are mined yearly. Probably 10% of this total is lost in treatment of the ore to produce the concentrate, and a further 10% is lost in making pig lead. The amount of lead discharged into the environment is equal to the amount weathered from igneous rocks. In global lead level terms, the power storage battery industry may have a relatively low impact on the environment because about 80% of all batteries are recycled.

2.1.1.1.1 Exposure

Lead is present in tap water as a result of dissolution from natural sources or from household plumbing systems containing lead in pipes. The amount of lead from the plumbing system that may be dissolved depends on several factors, including acidity (pH), water softness, and standing time of the water [3]. Food can be contaminated by naturally occurring lead in the soil as well as by lead from sources such as atmospheric fallout or water used for cooking.

The total intakes and uptakes of lead from all sources are 29.5 and 12.5 µg/d, respectively, for children and 63.7 and 6.7 µg/d, respectively, for adults in urban areas [4]. The relative contribution of water to average intake is estimated to be 9.8% and 11.3% for children and adults, respectively. The total intake of lead from three of the four major sources—air, food, and dust—appears to have dropped significantly since the mid-1980s as a result of regulatory and voluntary actions to control lead from air (via gasoline) and food (via cans).

Other sources of lead intake include ceramic ware, activities involving arts and crafts, peeling paint, and renovations resulting in dust or fumes from paint [5]. No allowance was made for the contribution of lead from these sources, because they occur on a highly sporadic basis and because no quantitative data are available. It has been pointed out [5] that old paint has been an important source of excess lead intake for inner-city children living in older housing stock in the United States. Although the lead pollution from mining activities presents a relatively localized problem, its magnitude is significant, and particularly on the water pollution side it is compounded by the occurrence of other heavy metals. The obvious danger of pollution from smelting operations has long been recognized. Pollution control practices, however, leave a great deal to be desired. Primary smelters process the ore material and are usually large but few in number, whereas secondary smelters process scrap from old batteries, cable sheathing, etc. and represent more dispersed point sources of heavy metal pollution.

2.1.1.1.2 Health Effects

Lead can be absorbed by the body through inhalation, ingestion, dermal contact (mainly as a result of occupational exposure), or transfer via the placenta. In adults, approximately 10% of ingested lead is absorbed into the body. Young children absorb from 40% to 53% of lead ingested from food. Once lead is absorbed, it enters either a “rapid turnover” biological pool with distribution to the soft tissues (blood, liver, lung, spleen, kidney, and bone marrow) or a “slow turnover” pool with distribution mainly to the skeleton [6]. Of the total body lead, approximately 80–95% in adults and about 73% in children accumulate in the skeleton. The biological half-life of lead is approximately 16–40 days in blood [6] and about 17–27 years in bones [6].

2.1.1.1.3 *Acute and Chronic Exposure*

Perhaps no other metal, not even arsenic, has had its toxicology so extensively studied as has lead. Lead poisoning has been actually linked to the fall of the Roman Empire. The high lead content in bones from the roman period supports the hypothesis that the use of lead containers for wine and other liquids, the use of lead water pipes, and lead-containing ceramic glazing of earthenware containers contributed to the decimation of the ruling class, who were more able to afford the lead containers [7]. The lead poisoning of children has been linked to contemporary earthenware glazed surfaces and pigments of older paints. The toxicology of lead has been extensively studied. Inorganic lead is a general metabolic poison and enzyme inhibitor (like most of the heavy metals). Organic lead is even more poisonous than inorganic lead. The earliest symptoms of lead poisoning seem to be psychical (e.g., excitement, depression, and irritability). Young children are particularly affected and can suffer mental retardation and semipermanent brain damage. One of the most insidious effects of inorganic lead is its ability to replace calcium in bones and remain there to form a semi-permanent reservoir for long-term release well after the initial absorption. The usual indicator of the degree of inorganic lead poisoning in humans is the content of this element in whole blood. Different authorities suggest safety levels in the range of 0.2–0.8 ppm. The figure 0.2 ppm seems to reflect a worldwide minimum. The disturbing fact is that the natural levels in human blood are already very close to what is considered a reasonable toxicological limit, not leaving us with any margin for exposure to lead.

Lead is a cumulative general poison, with fetuses, infants, children up to six years of age, and pregnant women (because of their fetuses) being most susceptible to adverse health effects. Lead can severely affect the central nervous system. Overt signs of acute intoxication include dullness, restlessness, irritability, poor attention span, headaches, muscle tremor, hallucinations, and loss of memory [8], with encephalopathy occurring at blood lead levels of 100–120 $\mu\text{g dL}^{-1}$ in adults and 80–100 $\mu\text{g dL}^{-1}$ in children. Signs of chronic lead toxicity, including tiredness, sleeplessness, irritability, headaches, joint pain, and gastrointestinal symptoms, may appear in adults with blood lead levels of 50–80 $\mu\text{g dL}^{-1}$ [8]. After one or two years of exposure, muscle weakness, gastrointestinal symptoms, lower scores on psychometric tests, disturbances in mood, and symptoms of peripheral neuropathy were observed in occupationally exposed populations at blood lead levels of 40–60 $\mu\text{g dL}^{-1}$ [9]. At levels of 30–50 $\mu\text{g dL}^{-1}$, there were significant reductions in nerve conduction velocity. Renal disease has long been associated with lead poisoning; however, chronic nephropathy in adults and children has not been detected below blood lead levels of 40 $\mu\text{g dL}^{-1}$. Finally, it has been demonstrated that interactions between calcium and lead were responsible for a significant portion of the variance in the scores on general intelligence ratings, and that calcium had a significant effect on the deleterious effect of lead [10]. Several lines of evidence demonstrate that both the central and peripheral nervous systems are principal targets for lead toxicity. These include subencephalopathic neurological and behavioral effects in adults and electrophysiological evidence of both central and peripheral effects on the nervous system in children with blood lead levels well below 30 $\mu\text{g dL}^{-1}$. The carcinogenicity of lead in humans has been investigated in several epidemiological studies of occupationally exposed workers [11]. The International Agency for Research on Cancer considered the overall evidence for the carcinogenicity of lead to humans to be inadequate [11].

2.1.1.2 **Cadmium**

Cadmium is a silvery-white, lustrous, but tarnishable metal; it is soft and ductile and has a relatively high vapor pressure. Cadmium is nearly always divalent; chemically it closely resembles zinc and occurs in almost all zinc ores by isomorphous replacement [12]. Cadmium is found in natural deposits as ores containing other elements. The greatest use of cadmium is primarily for electroplating, paint pigments, plastics, silver–cadmium batteries, and coating operations, including transportation equipment, machinery and baking enamels, photography, and television phosphors. It is also used in nickel–cadmium batteries, in solar batteries, and in pigments [13]. In one review, it was noted that the use of cadmium products has expanded in recent years at a rate of 5–10% annually, and the

potential for further growth is very high [14]. The whole world's annual production of cadmium is around 20,000 tons. Discharge of cadmium into natural waters is derived partly from the electroplating industry, which accounts for about 50% of the annual cadmium consumption in the USA. Other sources of water pollution are the nickel–cadmium battery industry and smelter operations, which are more likely to be fewer in number but of a greater point source significance, often affecting the environment at distances of a 100 km order of magnitude [15].

2.1.1.2.1 Occurrence

Cadmium is a relatively rare element. It is uniformly distributed in the Earth's crust, where it is generally estimated to be present at an average concentration of between 0.15 and 0.2 mg kg⁻¹ [16]. Cadmium occurs in nature in the form of various inorganic compounds and as complexes with naturally occurring chelating agents; organocadmium compounds are extremely unstable and have not been detected in the natural environment. Industrial and municipal wastes are the main sources of cadmium pollution. The solubility of cadmium in water is influenced to a large degree by the acidity of the medium. Dissolution of suspended or sediment-bound cadmium may result when there is an increase in acidity [17]. The need to determine cadmium levels in suspended matter and sediments in order to assess the degree of contamination of a water body has been pointed out. The concentration of cadmium in unpolluted fresh waters is generally less than 0.001 mg L⁻¹ [16]; the concentration of cadmium in seawater averages about 0.00015 mg L⁻¹ [17]. Surface waters containing in excess of a few micrograms of cadmium per liter have probably been contaminated by industrial wastes from metallurgical plants, plating works, plants manufacturing cadmium pigments, textile operations, cadmium-stabilized plastics, or nickel–cadmium batteries, or by effluents from sewage treatment plants [17].

High concentrations of cadmium in air are associated with heavily industrialized cities, notably those having refinery and smelting activities [16], where levels may be several hundred times those found in noncontaminated areas [18]. According to the earlier (1969) data from the U.S. National Air Sampling Network, the annual average cadmium concentrations at 29 nonurban stations were all less than 0.000003 mg m⁻³; those for the 20 largest cities ranged from 0.000006 to 0.000036 mg m⁻³ [18].

The presence of cadmium in vegetation may arise from the deposition of cadmium-containing aerosols directly on plant surfaces and by the absorption of cadmium through roots. Plants vary in their tolerance to cadmium in soil and in the amounts they are able to accumulate. Certain shellfish, such as crabs and oysters, may concentrate cadmium to extremely high levels in certain tissues, even if they inhabit waters containing low levels of cadmium. Reported concentrations of cadmium in foodstuffs vary widely; concentrations in most foods average about 0.05 mg kg⁻¹ on a wet-weight basis. Other fresh meats generally contain less than 0.05 mg kg⁻¹; cadmium concentrations in fish are usually less than 0.02 mg kg⁻¹ [18]. In cadmium-polluted areas, cadmium levels may be significantly elevated; rice and wheat from contaminated areas of Japan have been found to contain concentrations near 1 mg kg⁻¹, at least a factor of 10 higher than those for most parts of the world [18].

2.1.1.2.2 Health Considerations

Cadmium is not at present believed to be an essential nutrient for animals or man. Several studies on human subjects indicate that 4–7% of a single dose of ingested cadmium is absorbed from the intestine. The absorption of cadmium nitrate or cadmium chloride in animal studies ranged from 0.5% to 3% [18]. The total amount absorbed by humans has been estimated as 0.0002–0.005 mg day⁻¹ [19].

Absorbed cadmium accumulates mainly in the renal cortex and liver. The pancreas, thyroid, gall-bladder, and testes can also contain relatively high concentrations. Several studies suggest that accumulation of cadmium in the human body is a function of age [20]; one author claims that there is a 200-fold increase in the cadmium content of the body in the first three years of life, and that in this early period humans accumulate almost one-third of their total body burden. Cadmium accumulates with age until a maximum level is reached at about age 50; the total body burden of a person of 50 years of age ranges from 5 to 40 mg. About half the body burden is found in the kidneys and

liver; the cadmium concentration of the cortex of the kidneys ranges from 0.005 to 0.1 mg g⁻¹. Concentrations of cadmium in the renal cortex are normally 5–20 times those in the liver [17].

2.1.1.2.3 Toxic Effects

Due to its acute toxicity studied only recently, cadmium has joined lead and mercury in the most toxic “Big Three” category of heavy metals with the greatest potential hazard to humans and the environment. Cadmium is one of the metals most strongly absorbed by living cells accumulated by vegetation. It is also among the most toxic to living organisms and more likely to leach from industrial wastes. The acute oral lethal dose of cadmium for humans has not been established; it has been estimated to be several hundred milligrams [21]. Doses as low as 15–30 mg [21] from acidic foodstuffs stored in cadmium-lined containers have resulted in acute gastroenteritis. The consumption of fluids containing 13–15 mg of cadmium per liter by humans has caused vomiting and gastrointestinal cramps.

Acute cadmium poisoning has occurred following exposure to fumes during the melting or pouring of cadmium metal [22]. Fatalities have resulted from a 5 h exposure to 8 mg m⁻³, although some individuals have recovered after exposure to 11 mg m⁻³ for 2 h. Acute pneumonitis resulted from inhalation of concentrations between 0.5 and 2.5 mg m⁻³ for 3 days. Symptoms of acute poisoning include pulmonary edema, headaches, nausea, vomiting, chills, weakness, and diarrhea. Cadmium has been established as a very toxic heavy metal. A disease known as “Itai-Itai” in Japan is specifically associated with cadmium poisoning, resulting in multiple fractures arising from osteomalacia [23]. Symptoms of the disease, which occurred most often among elderly women who had many children, are the same as those of osteomalacia (softening of the bone); the syndrome is characterized by lumbar pain, myalgia, and spontaneous fractures with skeletal deformation. It is accompanied by the classical renal effects of industrial cadmium poisoning: proteinuria, and often glucosuria, and aminoaciduria [18].

Cadmium tends to accumulate in the human body (30 mg in an average American male), with 33% in the kidneys and 14% in the liver. Chronic cadmium poisoning produces proteinuria and causes the formation of kidney stones. There is evidence of a link between cadmium and hypertension. The main problem with cadmium in humans appears to be that the body seldom excretes as much cadmium as is absorbed. There is little general agreement about acceptable safety limits for cadmium intake. In the USA, the safety level of cadmium in drinking water has been set at 10 ppb. Sampling of surface waters revealed some dangerously high cadmium levels. Chronic exposure to airborne cadmium results in a number of toxic effects; the two main symptoms are lung emphysema and proteinuria [22]. Emphysema appears after approximately 20 years of exposure; levels of exposure that result in disability have not been systematically determined. It has been proposed that the minimum critical level of cadmium in the kidney required to produce renal tubular damage is approximately 0.2 mg g⁻¹ [24]. The World Health Organization (WHO) has recommended that the provisional permissible intake of cadmium not exceed 0.4–0.5 mg per week or 0.057–0.071 mg d⁻¹ [24].

2.1.1.3 Mercury

Mercury is a dense, silvery-white metal that melts at –38.9°C. Mercury is present in the Earth’s crust at an average concentration of 0.08 mg kg⁻¹; cinnabar (mercury[II] sulfide, HgS) is the most common mercury ore [25]. Igneous, metamorphic, and sedimentary rocks contain mercury at concentrations up to 0.25, 0.40, and 3.25 mg kg⁻¹, respectively [25]. Mercury and its compounds are used in dental preparations, thermometers, fluorescent and ultraviolet lamps, and pharmaceuticals, and as fungicides in paints, industrial process waters, and seed dressings. The pulp and paper industry also consumes mercury in significant amounts in the form of phenyl mercuric acetate, a fungicide, and in caustic soda, which may contain up to 5 mg kg⁻¹ as an impurity.

2.1.1.3.1 Occurrence

Many mercury compounds are volatile, and most decompose to form mercury vapor. Elemental mercury has a substantial vapor pressure even at ambient temperatures but, except at elevated

temperatures, does not react readily with oxygen in air. Mercury can exist as univalent and divalent ions. Mercury(I) is always in 2+, and all of its compounds are the dimeric form. Mercury(II), Hg^{2+} , forms both covalent and ionic bonds; HgCl_2 , for example, is covalent. This causes a relatively low solubility of HgCl_2 in water and higher solubility in organic solvents. Mercury(II) can also form complexes by accepting pairs of electrons from ligands. The covalent property of mercury(II) allows a stable mercury-carbon bond and the formation of organometallic compounds. The organomercury salts are soluble in organic solvents, and compounds such as dimethyl mercury, $(\text{CH}_3)_2\text{Hg}$, can easily be separated from inorganic salts and even from HgCl_2 , as HgCl_2 can first be complexed to form 2+ with excess chloride. The distribution of mercury between the three oxidation states is determined by redox potential, pH, and the anions present.

Mercury can enter the atmosphere by simple transport as metallic mercury vapor or as volatilized organic mercury compounds. The formation of volatile organomercurials may occur through microbial, animal, or plant metabolic activity. These natural processes result in the constant circulation of significant quantities of mercury in the atmospheric environment. The US Environmental Protection Agency (EPA) has estimated rural concentrations of mercury in air to be $0.000005 \text{ mg m}^{-3}$, urban concentrations $0.00003 \text{ mg m}^{-3}$, and indoor concentrations $0.0001\text{--}0.0002 \text{ mg m}^{-3}$; the average atmospheric concentration was estimated at $0.00002 \text{ mg m}^{-3}$, and it was stated that atmospheric concentrations are unlikely to exceed an average value of $0.00005 \text{ mg m}^{-3}$ [26]. Mercury in air can be washed out by rain. In industrial areas, mercury concentrations as high as 0.0002 mg L^{-1} have been reported in rain. In most surface waters, $\text{Hg}(\text{OH})_2$ and HgCl_2 are the predominant mercury species. In reducing sediments, however, most of the mercury is immobilized as the sulfide. Concentrations of mercury in surface and drinking waters are generally below 0.001 mg L^{-1} [26]. The presence of higher levels of mercury in water is due to effluents from the chlor-alkali industry, the pulp and paper industry, mining, gold, and other ore-recovering processes, and irrigation or drainage of areas in which agricultural pesticides are used.

Inorganic mercury in sediments, under anaerobic conditions, can be transformed by microorganisms into organic mercury compounds, the most common of which is methyl mercury [27]. These compounds can readily associate with suspended and organic matter and be taken up by aquatic organisms. Methyl mercury has high affinity for lipids and is distributed to the fatty tissues of living organisms [28]. Although methyl mercury is estimated to constitute only 1% of the total mercury content of water, more than 90% of the mercury in biota is in the form of methyl mercury [28]. It has been estimated that about 5000 tons of mercury are annually released into the environment by man's activities. Mercury is readily scavenged by organic matter. Mercury salts from industrial effluents deposit in river or lake sediments and are then acted upon by anaerobic bacteria, which convert them into toxic methyl mercury and dimethyl mercury. It is in the hydrosphere that the effects of mercury pollution are most significant. Soluble mercury is readily incorporated into organisms in the aquatic environment and ultimately finds its way into higher members of the food chain such as man. The progress of mercury through the food chain successively increases its concentration to such an extent that natural levels in some commercial fish are close to, or exceed, the lowest level now set by the health authorities in many countries. It is therefore obvious that a small additional "pollution" component can be sufficient to cause a public health hazard under certain circumstances. This situation has already been reached for mercury and lead and may soon apply to cadmium. Analyses of the Greenland ice cap revealed that while mercury levels worldwide had been constant since 800 B.C., since 1950 the amounts present seem to have doubled.

2.1.1.3.2 Health Effects

Absorption of metallic mercury following ingestion is negligible; less than 0.01% of an administered dose of metallic mercury was absorbed in animals, for example. In humans, accidental ingestion of several grams of metallic mercury increased blood mercury levels [29], but only rarely did doses of 100–500 g cause clinical illness (stomatitis and diarrhea). Soluble inorganic mercury(II) salts are absorbed to a limited extent, 7–15% in humans, and sparingly water-soluble mercury(I)

salts are absorbed to an even lesser degree. The mercury(I) ion can be biotransformed to the mercury(II) ion *in vivo*, however. Ingested organic mercury, on the other hand, is readily absorbed [30]; 95% or more is absorbed in humans. Absorption depends on particle size, solubility, and rate of decomposition of the salts in biological fluids. A fraction of inhaled mercury salts will be cleared to the alimentary tract and absorbed by ingestion. Generally, aerosols of inorganic mercury compounds are absorbed to a lesser degree than is mercury vapor.

2.1.1.3.3 *Distribution and Metabolism*

The world's annual consumption of mercury averages about 10,000 tons, and about half of this total is used in the production of chlorine for bleaching paper pulp. As a result of the established mercury threat, the largest man-handling of mercury in chlorine manufacture is being limited by introducing alternative technologies that do not employ mercury electrodes. The next largest mercury consumption (approximately 35%) is in the production of switch gear and batteries.

Inorganic mercury compounds are rapidly accumulated by the kidney, the main target organ for these compounds. Mercury in the kidneys is in the form of a metallothionein-like complex. Binding of the mercury by the protein, metallothionein, is enhanced in the presence of cadmium. Phenyl and methoxyethyl mercuric salts rapidly degrade to mercuric salts and distribute as such in the bodies of humans and animals. The toxicity of these organomercurials is dependent on the rate of their conversion (biotransformation) to inorganic mercury; because this conversion is rapid, the toxicity of these compounds in cases of chronic exposure is similar to that seen after inorganic mercury exposure. Elemental mercury vapor that is inhaled rapidly diffuses through the alveolar membrane; in the body, it is oxidized to mercuric ions, which produce the toxic effects.

Absorption of methyl mercury from food (bound to protein) or water (as chloride salt) is almost complete both in animals and in humans. Methyl mercury has considerable stability in the body and circulates for a time unchanged in the blood. It is distributed in high concentrations to the kidney and somewhat less to the liver. In the kidney, 40% is present in the inorganic form. In humans, methyl mercury has a ratio of 20:1 between red blood cells and plasma, in contrast to the 1:1 ratio after exposure to inorganic or phenyl mercury [26]. The most reliable index of exposure to methyl mercury and of retention in the central nervous system is the finding of methyl mercury in red blood cells. Hair mercury levels reflect past exposure and are dependent on the rate of hair growth. There is an almost linear relationship between the amount of methyl mercury in blood and that in the hair that was formed during exposure; the ratio of hair to blood levels has been consistently found in the range 230–300:1 [26]. At steady state, the level of mercury in blood is proportional to the daily intake of methyl mercury; the constant of proportionality for a 70 kg adult has been estimated to be between 0.3 and 1.0 (units of days per liter).

2.1.1.3.4 *Toxicity*

With the possible exception of lead, mercury as a pollutant has been studied more extensively than any other trace element during the past three decades. Although it had been known for many centuries that mercury is poisonous to animals and humans, it was not until the late 1950s that its extreme toxicity to humans was appreciated as it made headlines worldwide. In 1953, the mysterious death of 52 persons living in fishing villages along Minamata Bay in Japan was unmistakably linked with mercury poisoning. High levels of mercury originating from the nearby plastics factory were found in the shellfish eaten by the villagers. The “minamata disease,” mercury poisoning, has been linked to many more deaths around the globe ever since and symptoms of mercury poisoning crippled countless more. Advanced analytical methods made it possible only relatively recently to monitor low levels of mercury in the environment, which, however, are sufficient to cause these serious problems on the large scale.

A particularly disturbing feature of mercury poisoning is that the effects are not immediately obvious. Methyl mercury is particularly toxic because it readily passes from the bloodstream into the cerebellum and cortex, causing damage that is symptomized by numbness, awkwardness of gait,

and blurring vision. Clinical tests to determine mercury poisoning are based mainly on the levels of this element in whole blood. Identifiable symptoms of mercury poisoning occur with levels of 0.2–0.6 ppm. Such levels would be reached by a daily intake of 0.3–1.0 mg of mercury by a healthy man. The WHO proposed an acceptable daily intake (ADI) of 0.3 mg Hg, of which not more than 0.2 mg should be in the form of methyl mercury. Since most of the environmental mercury is derived from natural sources, man's addition to this load is of critical importance. The appearance, character, and extent of the toxic effects of mercury depend on a number of factors: the chemical form of the mercury; the mercury compound and its ionization potential; the dose, duration of exposure, and the route of administration; and the dietary levels of interacting elements, especially selenium [30]. When given in acute massive doses, mercury, in whatever chemical form, will denature proteins, inactivate enzymes, and cause severe disruption of any tissue with which it comes into contact in sufficient concentration.

The two major responses to mercury poisoning involve neurological and renal disturbances. The former is characteristic of poisoning by methyl and ethyl mercuric salts, in which liver and renal damages are of relatively little significance. The latter is characteristic of inorganic mercurial poisoning. In general, however, acute lethal toxic doses by ingestion of any form of mercury will result in the same terminal signs and symptoms, which consist of shock, cardiovascular collapse, acute renal failure, and severe gastrointestinal damage. After acute administration of ionizable inorganic salts of mercury to animals or humans, the highest levels of mercury are found in the kidney; although acute oral poisoning results primarily in hemorrhagic gastritis and colitis, the ultimate damage is to the kidney. Clinical symptoms of acute intoxication include pharyngitis, dysphagia, abdominal pain, nausea and vomiting, bloody diarrhea, and shock. Later, swelling of the salivary glands, stomatitis, loosening of the teeth, nephritis, anuria, and hepatitis occur. Ingestion of 500 mg mercuric chloride causes severe poisoning and sometimes death in humans. Acute exposure results from inhalation of air containing mercury vapor in the range 0.05–0.35 mg m⁻³. Exposure for a few hours to a concentration of between 1 and 3 mg m⁻³ may give rise to pulmonary irritation and destruction of lung tissue and occasionally central nervous system disorders [30]. Chronic exposure occurs in persons occupationally exposed to large amounts of mercury on occasion and as a result of prolonged therapeutic use. Alkyl compounds of mercury are the most toxic to humans, producing illness, irreversible neurological damage, or death from the ingestion of milligram quantities [31]. Outbreaks of poisonings by these organic derivatives have been the result of accidents or of environmental contamination in a number of countries: Iraq, Guatemala, Pakistan, Japan (Minamata and Niigata), and the USA [31].

Symptoms may occur weeks or months after exposure to toxic concentrations of either methyl mercury or ethyl mercury. Therefore, no clear distinction between acute and chronic symptomatology can be made. In cases of severe poisoning, pronounced weight loss can occur with or without intestinal symptoms. Neurological symptoms include mental deterioration, rigidity and hyperkinesia, and salivation and sweating. Alkyl mercury readily crosses the placenta unchanged and concentrates in fetal tissues. As a result, infants born to exposed mothers may suffer from mental retardation, cerebral palsy, and convulsions. The fetus is far more sensitive to methyl mercury poisoning than is the child, and children below 10 years of age are more susceptible than adults. Although methyl mercury acts on basic genetic systems such as the spindle fiber mechanism and DNA, its mutagenic potential appears to be small. No evidence for genetic, teratogenic, or carcinogenic effects has yet been described for inorganic mercury.

2.1.1.4 Chromium

As any other transition metal, chromium can be found at a degree of oxidation ranging from (–II) to (+VI). However, the most common oxidation states of chromium are (0), (III), and (VI). In natural deposits, chromium is present in complex cubic isomorphous minerals called spinel. Most of the chromium found in nature is in its trivalent state (the most stable one), but small amounts of the hexavalent form have been found along with the divalent oxidation state. Chromium is used in many

industrial applications. It can be either used melted with other metals to produce alloys or plated. Chromium steel alloys provide high corrosion resistance and good hardenability. Other applications of chromium range from tanning agents, paint pigments, and catalysts to impregnation solution for wood or photography. The world production of chromite ore is several millions of tons per year. Ferrochromite is obtained by direct reduction of the ore while chromium metal is produced either by chemical reduction (aluminothermic process) or by electrolysis of either CrO_3 or chrome alum solutions.

2.1.1.4.1 Chemical Pathways

Chromium concentrations in both air and soil are subject to large variations. In air the concentrations range from 0.3 ng m^{-3} in remote sites to 50 ng m^{-3} in urban areas, and in soil they vary from traces to 250 mg kg^{-1} , where it may be from phosphate fertilizers. Chromium concentrations in natural waters are very limited by the low solubility of Cr(III) oxides. Thus a major part of chromium in waters is in the hexavalent state. Main contaminations are generated by industrial wastewaters. Since the trivalent state is predominant in soils, it is unlikely that even heavily polluted farmland would result in chromium accumulation in the food chain via plants. No common plant used as animal feed or food has been reported with a tendency to concentrate chromium.

Q1

2.1.1.4.2 Clinical Effects

Chromium was recognized to be a hazardous element in the early years after it was discovered. No reports indicate that chromium salts (+III) have severe toxic effects. Hexavalent chromium is considered to be lethal for a dose higher than 3 g for adult humans. The first symptoms are vomiting and persisting diarrhea. After a week, hemorrhagic diathesis and epistaxis are commonly observed. Convulsions occur during the final stages of the illness. Repeated occupational inhalation of hexavalent chromium compounds causes perforations of the nasal septum and skin ulceration "chrome holes." The sense of smell and acute irritative dermatitis or allergic eczematous dermatitis have frequently been reported in case of chronic exposure to chromic acid vapors as well as an increased incidence of cancer in the respiratory organs. Bronchial asthma due to chromate dust or chromic acid fumes has been experienced by a number of workers. Environmental contamination with chromium seems trivial compared to mercury or cadmium. Nevertheless, severe toxic effects on plants have been reported at Cr(VI) concentrations of approximately 0.5 mg L^{-1} .

2.1.1.4.3 Monitoring and Legislations

It is accepted that monitoring both atmosphere and biological material from exposed workers is essential. Chromium concentrations can be determined using colorimetry, atomic absorption, or emission spectroscopy. The US Standards Institute listed a maximum acceptable concentration (MAC) of 0.1 mg m^{-3} for chromic acid. The U.S. National Institute of Occupational Safety and Health (US-NIOSH) makes a difference between noncarcinogenic Cr(VI) and carcinogenic Cr(VI). The time-weighted average values at a workplace are $25 \text{ } \mu\text{g m}^{-3}$ for airborne carcinogenic chromium and $50 \text{ } \mu\text{g m}^{-3}$ for noncarcinogenic chromium.

2.1.2 RADIONUCLIDES

2.1.2.1 Uranium

Uranium (U) is a hard, silvery-white amphoteric metal and a radioactive element. In the natural state, it consists of isotopes ^{238}U (99.28%), ^{234}U (0.006%), and ^{235}U (0.714%). Uranium occurs naturally in the +2, +3, +4, +5, or +6 valence states, but most commonly in the hexavalent form. In nature, hexavalent uranium is commonly associated with oxygen as the uranyl ion, UO_2^{2+} . There are over 100 uranium minerals: those of commercial importance are the oxides and the oxygeneous salts. Although uranium has a family of 15 radioisotopes, only three occur naturally. The radiation levels from all three are very low due to two factors: (1) the radiation they emit is not very penetrating

and is emitted at a low rate; and (2) the high density of uranium (1.7 times the density of lead and 2.5 that of steel) acts as a shield against its own radiations. Large quantities of natural uranium can therefore be handled without any special precautions such as shielding or remote handling. Uranium is present in water supplies as a result of leaching from natural deposits, its release in mill tailings, emissions from the nuclear industry, and the combustion of coal and other fuels. Phosphate fertilizers, which may contain uranium at concentrations as high as 150 mg kg^{-1} , may also contribute to the uranium content of groundwater.

2.1.2.1.1 Biological Pathways

Uranium occurs in the mammalian body in soluble form only as tetravalent uranium or hexavalent uranium in uranyl complexes. Both hexavalent and tetravalent uranium form complexes with carbonate ions and proteins in the body. Oxidation of tetravalent uranium to hexavalent uranium is likely to occur in the organism. Absorption of uranium salts may occur by inhalation or by ingestion; 95% of uranium retained in the body is deposited in bone. Excretion is mainly via the kidney. As all uranium isotopes are radioactive, the hazards of a high intake of uranium are twofold: chemical toxicity and radiological damage. There is no evidence that uranium has any metabolic function in the mammalian organism.

2.1.2.1.2 Chemical Toxicity

The critical organ for chemical toxicity is the proximal tubule of the kidney. Chemical injury reveals itself, in humans, by increased catalase excretion in urine and proteinuria. Such changes are likely to occur when the uranium concentration in the kidney exceeds 1 mg kg^{-1} . The concentration of uranium in the kidney is mainly dependent on the solubility of the uranium compound to which the individual is exposed. The limiting daily intake of uranium is in the order $1.5 \mu\text{g d}^{-1}$, and it is mainly derived from food items such as vegetables, cereals, and table salt. Occupational exposure involves the inhalation of dust particles of varying size and density containing uranium compounds with different solubility.

The most important effect of uranium is the damage to the kidneys. High doses of uranium cause tissue damage in the kidneys, leading to functional loss as indicated by failure to resorb urinary protein, glucose, catalase, phosphate, citrate, and creatinine, causing slow death by suppression of respiration. A high dosage of uranium also affects blood vasculature through the body. Capillary permeability, blood pressure, and edema may increase and clotting ability may decrease. Uranium may damage the capillary membrane, and it is also known to induce some damage to liver and muscle tissue. Its effects on the nervous system may be similar to those from poisoning by other heavy metals. A study of the chemical toxicity of uranium revealed that a body burden of 0.1 mg kg^{-1} of body weight produced a definite nephrotoxic effect. The toxic effects of uranium were reviewed by a panel of prominent uranium toxicologists in 1984 and are summarized in Table 2.1.

TABLE 2.1
Health Effects of Uranium

Health Effect	Uranium (kg) Body Weight (mgU kg^{-1})	Uranium (mg) in a 70 kg Person	Uranium Intake (mg) by a 70 kg Person
50% lethality	1.63	114	230
Threshold for permanent renal damage	0.3	21	40
Threshold for transient renal injury or effect	0.058	4.06	8.3
No effect	0.03	2.1	4.3

Q2

2.1.2.2 Radon

Radon-222 is a chemically inert gas formed through the radioactive decay of ^{226}Ra . Both are members of the ^{238}U decay series. Although a gas, radon deserves a mention here due to its toxic effects and stealthy presence in habitable structures. Radon is soluble in water, its solubility decreasing rapidly with an increase in temperature (510, 230, and 169 $\text{cm}^3 \text{kg}^{-1}$ at 0°C , 20°C , and 30°C , respectively) [32]. Radon is extremely volatile and is readily released from water.

Uranium and radium are present in varying amounts in all rocks and soils. Although most of the radon produced in soil from radium is retained in the Earth, where it decays, a small portion diffuses into the pore spaces and hence into the atmosphere. Other sources of radon include groundwater that passes through radium-bearing rocks and soils, traditional building materials such as wallboard and concrete blocks, uranium tailings, coal residues, and fossil fuel combustion.

2.1.2.2.1 Exposure

Radon is the major source of naturally occurring radiation exposure for humans. Exposure occurs via the ingestion of radon dissolved in water and the inhalation of airborne radon. A US survey estimated geometric mean radon levels in public water supplies, public groundwater supplies, and private wells of 2.5, 4.8, and 34 Bq L^{-1} . Public wells analyzed by King et al. [33] contained radon at an average concentration of about 40 Bq L^{-1} . Nazaroff et al. [34] reported a geometric mean radon concentration of 5.2 Bq L^{-1} in public well water supplies in the United States, based on population-weighted statistics. In Finland and Sweden, the population-weighted average for drinking water from private wells has been estimated at 60 and 38 Bq L^{-1} , respectively [35].

Outdoor radon concentrations vary seasonally and diurnally and are influenced by height above ground level and meteorological conditions such as wind speed and temperature [35]. Enhanced levels will be found in the vicinity of uranium mines and mill and tailings operations. Indoor radon levels are typically much higher and much more variable than outdoor levels. Radon entry into houses and other buildings is primarily from the soil or rock under the structures. Radon in water, building materials, and natural gas can also contribute to indoor levels [35], particularly in confined spaces with low air change rates (e.g., homes that have been tightly sealed for energy conservation).

The relationship between the concentration of radon in the water supply and the concentration of radon in indoor air depends on several factors, including the rate and type of usage of the water (e.g., drinking water, showers, and laundry), the loss or transfer of radon from the water to the air, and the characteristic ventilation of the house. Nazaroff et al. [34], based on measurements in U.S. homes and water supplies, estimated that public supplies derived from groundwater serving 1000 or more persons contribute about 2% to the mean indoor radon concentration for houses using these sources. In general, under normal conditions, the intake of radon from indoor and ambient air far surpasses the intake of radon from drinking water via both the ingestion and inhalation routes.

2.1.2.2.2 Health Effects

Radon consumed in water appears to rapidly enter the bloodstream from the stomach, perfusing all the cells of the body [36]. As it is lipid soluble, it does not distribute evenly throughout the body [37]. Clearance of radon from the bloodstream is relatively rapid, with a half-time on the order of minutes.

Hursh et al. [37] demonstrated that radon is removed from the body primarily through exhalation via the lung. Several studies have found that radon is removed from the body with a primary half-time of between 30 and 70 min, with a smaller component (possibly that associated with fatty tissue) having a half-time on the order of several hours. The rate of radon elimination from a resting person appears to be slower than that for a physically active person [36]. Most radon inhaled with indoor air is exhaled and remains in the lungs for only a short time. The radon daughter ^{218}Po is very reactive and electrostatically attracted to tiny particulates in air. These particulates are inhaled and deposited in the lung. Radon's daughters then decay sequentially, releasing damaging alpha and beta particles. Therefore, it is radon's progeny, not radon, that actually cause damage to the bronchial epithelium, because only the progeny remain in the lungs long enough to decay significantly.

Epidemiological data derived from underground miners of various metal ores have shown a relatively consistent relationship between lung cancer incidence and exposure to radon progeny [38]. Limitations of the miner studies include crude exposure estimates, inadequate follow-up periods, [38] and the inability to account for the confounding factor of cigarette smoking. Comparatively few epidemiological studies have investigated the exposure to natural background radon levels, and those that are available show no significant increase in lung cancer death rate from inhalation exposure to normally occurring levels of radon and radon progeny [38]. Also, there are no experimental or epidemiological data available that link ingested radon with any known health impacts in humans [38]. It has been concluded that there is no need to establish a MAC for radon in drinking water. However, anyone whose indoor air radon concentrations exceed acceptable levels (800 Bq m^{-1} as an annual average concentration in the normal living area) should investigate the possibility that their groundwater also contains high levels of radon. Individuals who attempt to remove radon from their water supply using point-of-use devices containing activated carbon should be cautioned regarding the difficulties of disposing of the used radioactive carbon.

2.1.3 ARSENIC POLLUTION

Highly poisonous arsenic is widely distributed in nature and occurs in the form of inorganic or organic compounds. The most toxic form of arsenic is its trivalent cation As^{+3} . Arsenic contamination has been reported from many parts of the world, including the USA, UK, Canada, and Australia; however, in terms of severity of the problem, Bangladesh tops the list, followed by India and China. In what has been dubbed “the largest poisoning in the history of mankind,” an estimated 40–60 million people suffer from different degrees of acute arsenic poisoning in Bangladesh and Eastern India alone. Well-known health problems caused by acute arsenic poisoning exist on a large scale in those parts of the world where high levels of arsenic are naturally present in a widespread aquifer tapped for drinking and irrigation.

2.1.3.1 Arsenic Speciation and Toxicity

Arsenic is a poisonous chemical that is widely distributed in nature and occurs in the form of inorganic or organic compounds. It is ranked as twentieth in abundance among the elements in the Earth's crust. Arsenic can exist in four valence states: -3 , 0 , $+3$, and $+5$. Under reducing conditions, arsenite, As(III) , is the dominant form; arsenate, As(V) , is generally the stable form in oxygenated environments. Elemental arsenic is not soluble in water. Arsenic salts exhibit a wide range of solubilities, depending on pH and ionic environment.

Inorganic compounds consist of water-soluble arsenite (As III), the most toxic form, and arsenate (As V), the less toxic form, and such pollutants have been associated with many health problems such as skin lesions, keratosis (skin hardening), lung cancer, and bladder cancer [39–41] (Figures 2.1 and 2.2). Organic arsenic species, abundant in seafood, are much less harmful to health, and are readily eliminated by the body. The release of arsenic in the environment occurs in a variety of ways through industrial effluents, pesticides, wood preservative agents, combustion of fossil fuels, and mining activity [39–41]. Indeed, arsenical insecticides have been used in agriculture for centuries, and particularly lead arsenate was quite extensively used in Australia, New Zealand, Canada, and the USA [41,42].

2.1.3.2 Arsenic-Contaminated Countries

Arsenic contamination has been reported from many parts of the world, including the USA, UK, Canada, and Australia; however, in terms of severity of the problem, Bangladesh tops the list, followed by India and China (Figure 2.3) [40]. In these countries, arsenic has been released in the groundwater by oxidation of the arsenopyrites/pyrites (arsenic is present in more than 200 mineral species, the most common of which is arsenopyrite) from the subsoil or oxyhydroxide reduction. It has been estimated that about one-third of the atmospheric flux of arsenic is of natural origin. Volcanic action is the most important natural source of arsenic, followed by low-temperature



FIGURE 2.1 Health effects of arsenic. Skin lesions and keratosis due to arsenic poisoning.

Q3



FIGURE 2.2 Health effects of arsenic. Skin lesions and keratosis due to arsenic poisoning.

volatilization. Inorganic arsenic of geological origin is found in groundwater used as drinking water in several parts of the world, for example Bangladesh [41].

Besides the drinking of contaminated groundwater, people in such countries use this water for crop irrigation. Therefore, arsenic compounds find their way into soils used for rice (*Oryza sativa*) cultivation through polluted irrigation water, and through historic contamination with arsenic-based pesticides [43]. Arsenic contamination poses a particular challenge, as this pollutant can enter plants through their phosphate transporter [44] and its contamination is invisible and has no taste or smell.

2.1.3.3 Clinical Effects

Skin disorders, including hyper/hypopigmentation changes and keratosis, are the most common external manifestations, although skin cancer has also been identified. Around 5000 patients have



Q4

FIGURE 2.3 Arsenic geographic occurrence.

been identified with As-related health problems in West Bengal (including skin pigmentation changes), although some estimates put the number of patients with arsenicosis at more than 200,000 [45]. In some areas in Bangladesh, groundwater arsenic concentrations can reach 2 mg L^{-1} (2 ppm) [41,46], whereas the WHO provisional guideline value for drinkable water is only 0.01 mg L^{-1} (10 ppb) [43]. An estimated Bangladesh population of 65 million is exposed to the threat of arsenic poisoning through drinking water [40], and surprisingly at least 32 million Americans consume water containing more than 2 ppb of arsenic. The US EPA is now considering a new standard in the range of 2–20 ppb.

2.2 METALS IN GROUNDWATERS

While the interest in groundwater has mainly focused on the supply of water, a shift of concern to groundwater quality has occurred. At present, the reservoir of freshwater found beneath the surface is gradually degrading due to man's activities. This is placing a strain on drinking water supply, especially in rural areas where tapping into the ground for water is a common practice. Regulations and introduction of standards concerning water quality have been counteracting this deterioration. However, groundwater contamination goes more frequently undetected or is largely undetectable due to heterogeneities underground, until the damage is widespread. Hope for the future lies in understanding the movement of water and contaminants in aquifers, a porous and permeable type of geological formation that holds and conducts the flow of groundwater.

Focus on inorganic contaminants has been relatively recent since organics are more used in industry and seem to have posed a more eminent problem. Many inorganic contaminants, specifically heavy metals, are toxic and pose a great health and environmental concern in quite low concentrations. Due to the progressive mobilization of heavy metals above the water table caused by man's increasing technological activities, the metals reach underground aquifers in increasing quantities. While some metals may be partially removed by ion exchange with the soil components before they reach the aquifer, the danger of contaminating the latter has been well established. The movement of heavy metals in aquifers depends on how the heavy metals act in aqueous environment. These considerations involve pH, hydrolysis, redox potential, and formation of complexes. Metal mobility generally tends to decline with pH where a solid, typically a metal hydroxide, a metal carbonate, a metal sulfide, or other complexes, becomes a more dominant phase.

2.2.1 HEAVY METALS IN AQUIFERS

The transport of solutes in porous materials, such as aquifers, can be considered as flow through a fixed volume element that can be reflected in the following mass balance:

$$\begin{aligned} (\text{net rate of change of mass within element}) = & (\text{flux of solute out of the element}) \\ & - (\text{flux of solute into the element}) \\ & \pm (\text{loss or gain of solute mass due to reaction}). \end{aligned}$$

Processes that dictate the flux in or out are advection and hydrodynamic dispersion. Advection is a component of solute movement attributed to transport by flowing groundwater. Dispersion refers to the spreading of the contaminant caused by the fact that not all of the contaminant actually moves at the same speed as the average linear velocity [47]. The average linear velocity (\bar{v}) is given by (v/n) , where v is the specific discharge and n is the porosity. The dispersion–advection equation, Equation 2.1, describes the transport of dissolved constituents that are reactive in saturated isotropic and porous media.

$$\frac{d}{dx} \left(T_x \frac{dh}{dx} \right) + \frac{d}{dy} \left(T_y \frac{dh}{dy} \right) = S \frac{dh}{dt} - R + L, \quad (2.1)$$

where $L = \frac{-K'h_{\text{source}} - h}{b'}$ [48].

This equation is based on the basic assumption that water in the aquifer tends to flow horizontally, that is, in the x and y directions, and vertically as leaks through confining beds. Hydraulic conductivity is the ability of an aquifer to transmit water and transmissivity (T) is the average transmission. T_x and T_y are the components of transmissivity, h is the hydraulic head, S is the storage coefficient, R is a sink/store term, and L is the leakage through the confining bed. K' is the vertical hydraulic conductivity of the confining bed, b' is the thickness, and h_{source} is the head in the reservoir on the other side of the confining bed.

A confined aquifer is overlain by a unit of porous material that tends to slow down water movement and its transmissivity will remain constant if the aquifer is both uniform in thickness and homogeneous in nature, which rarely is the case. To simplify the advection–dispersion further, the case of flow for nonreactive dissolved constituents in saturated, homogeneous isotropic material at steady state is taken. The advection–dispersion equation then becomes Equation 2.2:

$$D_1 \frac{d^2 C}{dl^2} - \bar{v}_l \frac{dC}{dl} = \frac{dC}{dt}, \quad (2.2)$$

where l is a curvy linear coordinate taken to be in the directions of the flow line, D_1 is the coefficient of hydrodynamic dispersion in the longitudinal direction, which depends on the dispersivity and properties of the porous media, and C is the solute concentration. Even with this simplified equation, the flow of contaminant with water through the aquifer is dependent on many variables.

A good visualization of the one-dimensional advection–dispersion equation is passing of a non-reactive tracer (C_0) through a homogeneous granular medium and looking at its relative concentration in the outflow as seen in Figures 2.4 and 2.5. The assumption of plug flow would have the solute exiting as a step function, indicated by the line marked “position of advection front.” In reality, mechanical dispersion and molecular diffusion cause flow to deviate from this; some molecules will move faster and some slower than the average linear velocity ($\bar{v} = Q/nA$), which is the flowrate divided by the product of porosity and cross-sectional area. The greater the distance of flow,

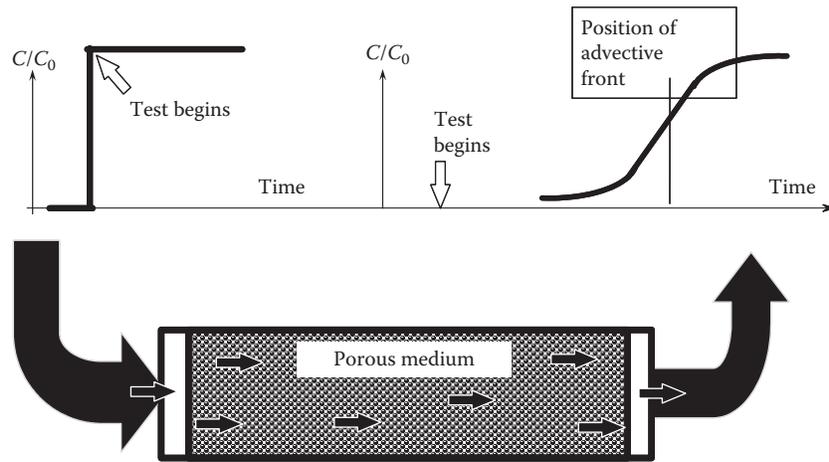


FIGURE 2.4 Experimental apparatus to illustrate dispersion in a column. The test begins with a concentration input of tracer $C/C_0 = 1$ at the inflow end. The relative concentration versus time function at the outflow characterizes dispersion in the column.

the greater the spread of the contaminant. At low velocities diffusion is dominant, and at high velocities dispersion is dominant.

As seen in Figure 2.6, diffusion of contaminants can translate to movement of great distances even through low-permeable rock, and can be considered an important factor in the movement of inorganic toxic contaminants. The overall spread of the species will depend on whether the source of contamination is continuous or instantaneous, as depicted in Figure 2.7. Despite the fact that the medium is isotropic, dispersion is anisotropic. It is stronger in the direction of flow than normal to it. The continuous contaminant spreads more from the source as time passes. The point source

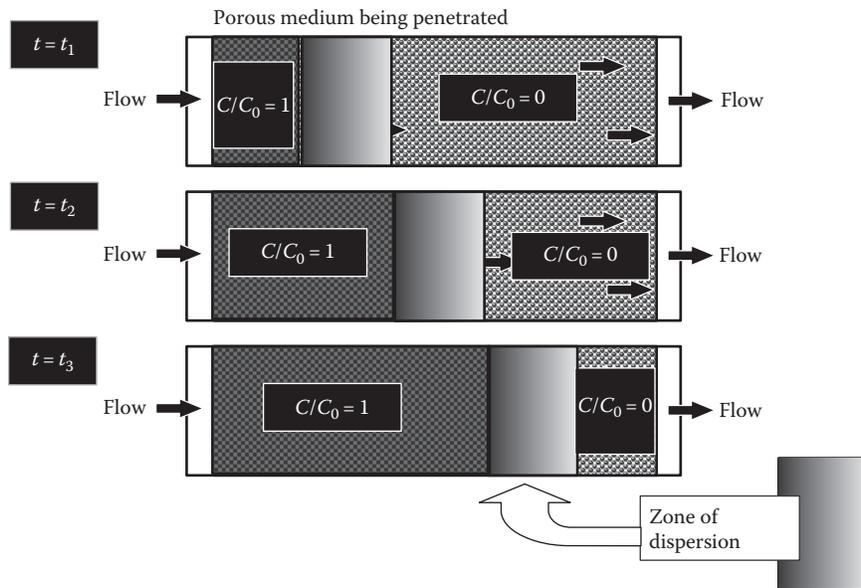


FIGURE 2.5 Schematic representation of dispersion within the porous medium at three different times. A progressively larger zone of mixing forms between the two fluids ($C/C_0 = 1$ and $C/C_0 = 0$) displacing one another.

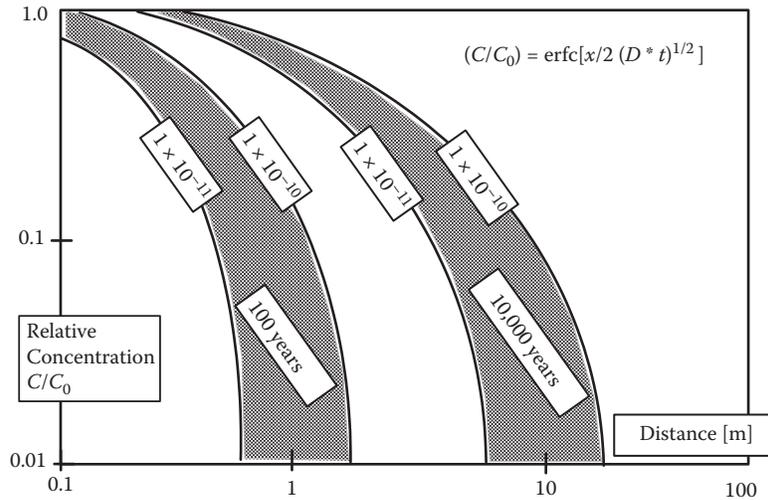


FIGURE 2.6 Positions of the contaminant front migrating by molecular diffusion away from a source where $C = C_0$ at $t > 0$. Migration times are 100 and 10,000 years.

contaminant contains a fixed mass, yet it is spread over a larger volume with time. Equations dictating this movement are used as a preliminary estimate. The contaminant concentration at a given point at a given time is by Equation 2.3:

$$C(x, y, z, t) = \frac{M}{8(\pi t)^{3/2} D_x D_y D_z} \frac{\exp - X^2 - Y^2 - Z^2}{4D_x t 4D_y t 4D_z t}, \tag{2.3}$$

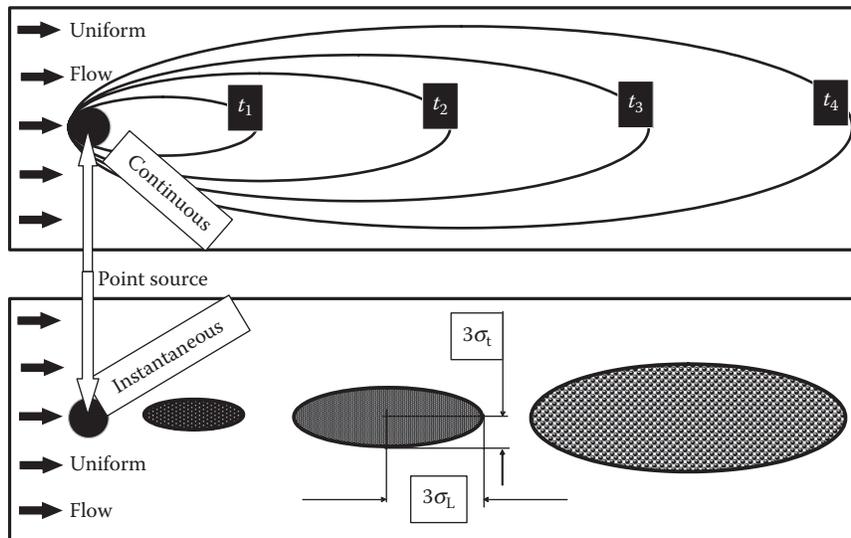


FIGURE 2.7 Spreading a tracer in a two-dimensional uniform flow field in an isotropic sand. (a) Continuous tracer feed with step-function initial condition; (b) instantaneous point source. (From Domenico, P.A. *Physical and Chemical Hydrogeology*. Wiley, Canada, 1990.)

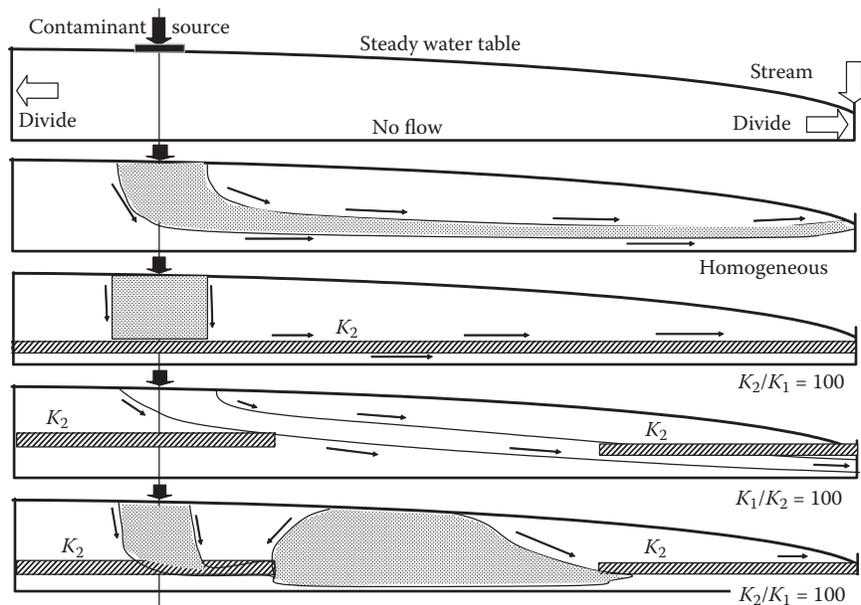
where M is the mass of the contaminant, D is the coefficient of dispersion in the x , y , or z direction, and $X = (x - vt)$, $Y = y$, $Z = z$ [49].

Density plays a key role in the downward movement of the contaminant. As density increases, relative to water, the contaminant plume which was shallow and close to the water table will sink into the groundwater. The assumption of homogeneous media is not true to reality; most geological media contain much heterogeneity. Figure 2.8 shows variations in the heterogeneous media. K_1 represents coarse gray sand and K_2 smaller grained sand in (c). A thin horizontal layer of higher conductivity extends through the original domain, most of the flow occurs in this layer, and overall travel time is one-fifth that in (d). Diagram (d) represents a discontinuous layer of flow conductivity, contamination moves the first and under the second lens, (e) indicates the discontinuity of a thin and high conductivity layer. The stratospheric differences are important to understand the movement of water in the aquifer.

Q5

Heterogeneities are usually determined by careful drilling and mapping. This is more applicable to large-scale heterogeneities. Changes in hydraulic conductivity can be attributed to small-scale heterogeneities such as changes in granular aquifers (changes in silt or clay content). Such heterogeneities cannot be determined from drillings from borehole to borehole. This fact leads to errors in dispersivity by up to an order of magnitude from those determined experimentally; hence dispersion plays a great role in contamination transport. Added complexity occurs when reactions within groundwater during transport of the contaminants occur, varying the concentrations substantially. These include adsorption/desorption reactions, solution precipitation reactions, oxidation/reduction reactions, ion-pairing or complexation reactions, and microbial cell synthesis. With the influence of reactions, specifically adsorption/desorption, the one-dimensional advection–dispersion equation becomes Equation 2.4 [49]:

$$D_1 \frac{d^2C}{dl^2} - \bar{v}_1 \frac{dC}{dl} + \frac{p_b}{n} \frac{dS}{dt} = \frac{dC}{dt} \tag{2.4}$$



Q6

FIGURE 2.8 Effect of layers and lenses on flow paths in shallow steady-state groundwater flow systems. (a) Boundary conditions; (b) homogeneous case; (c) single higher-conductivity layer; (d) two lower-conductivity lenses; (e) two higher-conductivity lenses. (From Freeze, A.R. and Cherry, J.A. *Groundwater*. Prentice-Hall, New Jersey, 1979.)

where p is the bulk mass density of the porous medium, n is the porosity, S is the mass of the chemical adsorbed on the porous medium, and $p/n (dS/dT)$ is the change in concentration due to adsorption/desorption following Equation 2.5.

$$-\frac{dS}{dt} = -\frac{dS^*dC}{dC dt} \quad \text{and} \quad -\frac{p_b dS}{n dt} = -\frac{p_b}{n} \frac{dS^*dC}{dC dt} \quad (2.5)$$

The term dS/dC represents partitioning of the contaminant between solution and solids. In the lab, the mass adsorbed per unit mass of dry solids is plotted against the concentration of the constituent in solution in a log/log graph. The resulting expression follows Equation 2.6:

$$\log S = b \log C + \log K \quad \text{or} \quad S = K_d C^b \quad (\text{Freundlich equation}), \quad (2.6)$$

which represents the relation between the mass of the solute species adsorbed (S) and the solute concentration (C) where K and b are constants that depend on solute species, type of porous media, and other conditions.

Reactions generally slow the rate with which the front of contaminants moves. The retardation equation for reactions is given by Equation 2.7 as

$$\frac{\bar{v}}{\bar{v}_0} = 1 + p_b \frac{K_d}{n} \quad (2.7)$$

where \bar{v} is the average linear velocity and \bar{v}_0 is the velocity of the $C/C_0 = 0.5$ point.

For example, for unconsolidated granular deposits, porosity typically is between 0.2 and 0.4 and average mass density is 2.65 for unconsolidated deposits. For the porosity, given the bulk mass densities (p) are 1.6–2.1 g cm⁻³, giving p_b/n values from 4 to 10 g cm⁻³. If $K_d = 1$ mL g⁻¹ then the flow of groundwater would be slowed by a factor of 5–11 times. If $K_d = 10$ mL g⁻¹ then the contaminating species would not move far from its point of input. A mixture of contaminants will separate into zones after time, given by \bar{v}/\bar{v}_0 for each species. These zones will travel at their own velocities. Later, when the contaminant discharge is discontinued, lower concentration water will pass through and adsorbed contaminant will be transferred into the liquid phase. If reactions are reversible, then in time, all evidence of contamination will be negligible; although this may be irreversible in a realistic time period when contaminants react slower than the actual movement of water, the retardation time will be even slower than that for the case of a fast reaction. Information on the movement of contaminants in the porous media is hard to come by and the use of the general retardation equation will yield errors in the prediction of the rates of migration of contaminants.

Heavy metals in contaminated water rarely occur at concentrations above 1 mg L⁻¹. Concentrations are low due to solubility, taking into account that other minerals are dissolved in this same water as well as the possibility of adsorption onto clay minerals or on hydrous oxides of iron and manganese or organic material. Isomorphous substitution of coprecipitation with minerals or amorphous solids can also be of some interest. Most heavy metals form hydrolyzed species and form complex species by combining with inorganic anions, such as HCO₃⁻, CO₃²⁻, SO₄²⁻, Cl⁻, F⁻, and NO₃⁻. Complexing with organic compounds may be important where present.

An equation that sums all amounts of the particular heavy metal complexed with various anions will give the total amount of metals present in all forms. If the total is known, then the amount of each species can be calculated using mass action equations. The hydrolyzed and inorganic species with mercury, for example, include HgOH⁺, Hg(OH)₂, HgCl₂, HgS, HgO, and Hg(HS)₂. In assessing the mobility of mercury and any other heavy metal, a knowledge of these and other species must

be looked at. As mentioned before, the increasing pH of groundwater leads to increased hydrolysis of the heavy metals. As their concentration in aquifers increases, so does their probability of complexing with anions present such as CN^- and HS^- . Heavy metal concentration can be calculated using concentration data obtained from laboratory analysis. Being able to predict the mobility of heavy metals in groundwater depends on the ease with which the concentration of the most dominant complexes formed can be predicted.

A generalized table of the mobilities of heavy metals in soil is shown in Table 2.2. This directly applies to aquifers since it is comparative and no numbers have been given.

Almost all the trace metals found in groundwater are influenced redox conditions, due to changes in the oxidation state of the metal complex. Redox conditions, in a way, may influence the concentration of trace metals in the solid phase of the porous medium that cause adsorption of the trace metal. The diagram of Eh versus pH for heavy metals in water shows the main stability regions of the particular heavy metal complexes.

In anaerobic groundwaters, insolubility of sulfide minerals can limit trace metals to very low concentrations. In groundwater, which is nonacidic and has a high concentration of dissolved inorganic carbon, the solubility of certain carbonate materials will, if equilibrium is achieved, limit the levels of trace metals at low concentrations, that is, Cd and Pb. This is true if excessive amounts of inorganic or organic substances, which tend to complex with heavy metals in water, are not present. Adsorption is the key mechanism that tends to keep concentrations far below those dictated merely by solubility. It occurs due to the presence of clay minerals, organic matter, crystalline solids, and other amorphous solids in the porous material. Certain oxides, for instance Fe and Mn, not only control but also enhance adsorption onto the medium for which they form a coat.

2.2.2 CASES AND REMEDIATION

In 1947, the city of Babylon in New York saw the beginning of land filling. Disposal included urban refuse, incinerated garbage, cesspool waste, and industrial refuse. The refuse was placed below the water table and the cesspool was treated and placed in lagoons. The surface sand aquifer was about 27.5 m thick and had a hydraulic conductivity of $1.7 \times 10^{-3} \text{ m s}^{-1}$. Contaminants in the aquifer included the major ions Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , Cl^- , NH_4^+ , and NO_3^- , heavy metals (particularly iron and manganese), and organic compounds. The Cl^- plume began 9.1 m below the water table and continued 12.1 m below. It did not react, so the mass transfer continued. The advection

TABLE 2.2
Relative Mobilities of Heavy Metals

Relative Mobility	Conditions			
	Oxidizing	Acid	Neutral (Alkaline)	Reducing
Very high			Se	
High	Se	Se, Hg		
Medium	Hg, As, Cd	As, Cd	As, Cd	Tl
Low	Pb, As, Sb, Tl	Pb, Bi, Sb, Tl	Pb, Bi, Sb, Tl, In	
Very low to immobile	Te	Te	Te, Hg	Te, Se, Hg, As, Cd, Pb, Bi, Tl

Source: Ferguson, J.E. *The heavy Elements: Chemistry, Environmental Impact and Health Effects*. Pergamon Press, New York, 1990.

velocity was determined at $2.9 \times 10^{-4} \text{ cm s}^{-1}$, which is the range expected for a sand aquifer. Dispersivities in the x , y , and z directions were 18.6, 3.1, and 0.6 m, respectively. Tracer tests estimated that the value in the x -direction would be 6 times those in the y -direction and the distance in the z -direction would be considerably smaller. The amount of Cl^- away from the source declined constantly, suggesting that the point source was continuous as indicated in Figure 2.7. Most of the nitrogen was present as NH_4^+ , indicating reducing conditions near the source. Mixing brought oxygen to the plume, producing $\text{NO}_3^- - \text{N}$ as the distance from the source increased. Tracking the nitrogen species allowed one to assess the redox conditions.

The area that was reduced is an explanation for the mobility of the heavy metals, iron and manganese. The Eh–pH diagram shows that Fe^{2+} was the stable form of iron at moderate reducing conditions and at a pH of 6; this was true for Mn^{2+} as well. The gradual increase in oxidizing conditions down the plume decreased mobility with the formation of solids (i.e., $\text{Fe}(\text{OH})_3$ and $\text{MnO}(\text{OH})$) [47]. It is a common practice to apply similar cases to areas that have minimum information: for instance, in the area around the Saint-Laurent Basin (Quebec, Canada), where four types of aquifers exist and one is similar to that mentioned in the Babylon case study. This is the one of unconsolidated sand and gravel deposits. Methods of remediation are available for removing inorganics from groundwater; they include chemical addition, removal of suspended solids, ion exchange, and polymeric binding with microfiltration. Changing the pH of water with chemical addition will cause the precipitation of heavy metals. To adjust acidic water, pass through a limestone bed mixed with lime slurries, add caustic soda (NaOH), or add soda ash (Na_2CO_3). To adjust alkaline water, bubble carbon dioxide in the water or add a strong acid. It is rare to have water that is too alkaline. Acids are added to adjust the pH back to normal after a high pH resulted in precipitation. Some metals do not precipitate out of solution at high pH and may need to be precipitated as a sulfide rather than a hydroxide, since they are soluble.

Heavy metals, such as hexavalent chromium, are soluble in water at high pH. This heavy metal is used in industrial operations and is not naturally found in groundwater. Its anthropogenic spread through natural aquifers could have serious health consequences in the affected population (movie: “Erin Brockovich” [51]). Hexavalent chromium is best reduced to its less soluble trivalent form for removal. The pH is reduced to pH 2, a chemical reducing agent such as sulfur dioxide is added, the pH is raised, and trivalent chromium is precipitated. Mercury is precipitated with sulfide addition. The lower treatability limit for mercury is 10–20 mg L^{-1} by sulfide precipitation, 1–5 mg L^{-1} with ion exchange, 1–10 mg L^{-1} with alum coagulation, 0.5–5 mg L^{-1} with iron coagulation, and 0.25 mg L^{-1} with activated carbon. Arsenic in groundwater may be present in arsenite (AsO_2^-) or arsenate (AsO_4^-). Oxygen will oxidize the arsenite to arsenate and most surface water contamination will be in the arsenate form. If contamination occurs in the deep and likely anaerobic aquifer, the arsenite or arsenic form should be somehow oxidized since arsenate is easier to remove. To remove arsenic, a floc must be formed. A polyvalent metallic coagulant must be added to produce a hydroxide floc. A relatively new method of precipitation is the addition of iron to water by electrochemical methods to enhance the precipitation of other inorganics. The system uses sacrificial electrodes to produce an insoluble ferrous ion, which absorbs and precipitates heavy metals.

Suspended solids can be removed by flocculation, chemical addition, and pH adjustment, which convert inorganic contaminants to no soluble forms. This together with one of several types of settlers can be employed in the removal of suspended solids. Ion exchange is the exchange of an ion with high affinity to the sorbent for an ion with lower affinity. All of the heavy metals, in an aqueous environment, are in the divalent or trivalent state, with the exception of hexavalent chromium. A home sodium-ion-exchange unit will remove all these compounds. Ion exchange is not cheap and the brine with heavy metals will have to be disposed of. The ionex process is put to the best use in low concentrations as the final treatment before potable use. Polymeric binding and microfiltration is a two-step method that selectively removes metals from groundwater. First the addition of a water-soluble polymer binds the metal sand, which is then followed by microfiltration. The favored polymer for heavy metals is polyethylene-imine at low pH.

2.3 HEAVY METAL POLLUTION SOURCES

Due to man's industrial activity the concentrations of some heavy metals have reached high levels, posing a danger to public health. Whereas the nature of domestic wastewater is relatively constant, the extreme diversity of industrial effluents calls for an individual approach to handling each type of industry and often entails the use of specific treatment processes. Therefore, a thorough understanding of the metal handling upstream production processes and of the overall production system organization is fundamental.

2.3.1 ACID MINE DRAINAGE

The major source of liquid waste in the mining industry is acid mine drainage (AMD). AMD is by far the most extensive and most severe environmental problem associated with mining activities, both current as well as past.

Precious metal and uranium mines contain sulfide minerals, either in the ore or in the surrounding waste rock. AMD is common in areas where mining openings intersect the water table and where rocks contain pyrite and/or other sulfides. When these sulfide minerals, particularly pyrite and pyrrhotite, are exposed to oxygen and water, a process of conversion of sulfide to sulfate takes place. Water in contact with these oxidizing minerals is made acidic and water carries with it toxic metals and elevated levels of dissolved salts. As the reactions proceed, temperature and acidity increase, resulting in an increased rate of reaction. Between pH levels of 2 and 4, bacteria and ferric iron catalyze the reaction rate. Rainfall and snowmelt flush the toxic solutions from the waste sites into the downstream environment. If acidic drainage is left uncollected and untreated, it could contaminate groundwater and local water courses, damaging the health of plants, wildlife, and fish and eventually posing a threat to human health, particularly through the toxicity of the heavy metals that it carries.

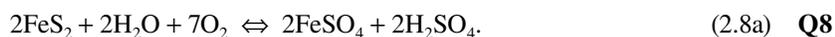
At active mine sites (and some inactive mine sites), mining companies operate comprehensive systems to collect and treat effluents and seepage from all sources. These facilities, when well operated and maintained, are sufficient to prevent downstream environmental impact. However, acid generation may persist for hundreds of years following mine closure. The problems are compounded by the demise and disappearance of the original mine operators.

The operation of treatment plants for very long periods of time is clearly not desirable and counter to the principles and goals of sustainable development. In addition, the conventional lime treatment process produces sludges that contain a very low percentage by weight of solids. In some severe cases, in a few decades the volume of lime sludge will exceed the volume of tailings or waste rock producing the acidic drainage.

2.3.1.1 Chemistry of Acid Mine Water

The principles of AMD generation are nowadays fairly well understood. Pyrite and other sulfide minerals on exposure to oxygen and water, and in the presence of oxidizing bacteria such as *Thiobacillus ferrooxidans*, oxidize to produce dissolved metals and acidity (sulfuric acid) according to the following steps [52].

The first of these reactions is the oxidation of pyrite:



The next step is the oxidation of ferrous ion to ferric ion:



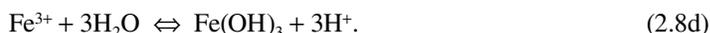
This process occurs very slowly at the low pH values found in acidic mine water. Below pH 3.5, the iron oxidation is catalyzed by the iron-oxidizing bacterium *Thiobacillus ferrooxidans*, and

in the pH range of 3.5–4.5, it may be catalyzed by a variety of *Metallogenium*, a filamentous iron-oxidizing bacteria. Other bacteria that may be involved in acid mine water formation are *Thiobacillus thiooxidans* and *Ferrobacillus ferrooxidans*.

The ferric ion further dissolves pyrite:



which in conjunction with reaction 2.8b constitutes a cycle for the dissolution of pyrite. At pH values much above 3, iron(III) precipitates as the hydrated iron(III) oxide:



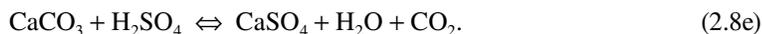
The beds of streams afflicted with AMD are often covered with “yellowboy,” an unsightly deposit of amorphous, semigelatinous $\text{Fe}(\text{OH})_3$. The most damaging component of acid mine water, however, is sulfuric acid. It is directly toxic and has other undesirable effects. While the devastation potential of AMD is very high, its dispersed nature and large areas involved in its generation represent a formidable problem in devising a suitably effective control of it. This is the reason why different techniques devised to treat AMD met with only little success. The techniques are based on the following methodologies:

Chemical: limestone/lime application to enhance alkalinity; sulfide precipitation or removal; application of bactericides.

Physicochemical: ion exchange barrier and application of a vegetative and/or geological membrane (cover) to prevent oxygen diffusion.

Biological: other than wetlands, not many biological treatments are known so far.

One approach to eliminating excess acidity involves the use of carbonate rocks. When acid mine water is treated with limestone, the following reaction occurs:



Unfortunately, because iron(III) is generally present, reaction 2.8d occurs as the pH is raised. The hydrated iron(III) oxide that forms as a result of elevated pH soon covers the particles of carbonate rock with a relatively impermeable layer. This armoring effect prevents further neutralization of the acid.

2.3.1.2 Extent of the Damage

The acidic water eventually interacts with other minerals and solubilizes heavy metals such as lead, copper, zinc, cadmium, and nickel that may even be present in minute quantities. Table 2.3 lists the amounts of major cations and anions contained in the mining water and solids of a typical AMD.

AMD is generated not only in and around abandoned mine sites but also at currently active operations. The principal sources of AMD at active mine sites are piles of waste rock containing pyrite, which is exposed to the atmosphere, to precipitation, and to springwater runoff. According to Kalin [53], 113 million cubic meters of contaminated water are produced annually from mining waste management areas in Canada. The flowrates of wastewater vary from 4 to 12,000 $\text{m}^3 \text{day}^{-1}$ and the level of contamination varies from parts per million (mg L^{-1}) levels to grams per liter levels [54]. Filion et al. [55] have estimated the cost of remedial action at operating and abandoned mine sites across Canada in the order of 4 billion Can\$ over the next 20 years. The rate of generation of heavy metal pollution is likely to further increase since the large-scale mining of low-grade ores uses the method of open pits, which often cut into the groundwater streams. During mining, the water is pumped out of the mine; however, once a mine is closed, water flows into the pit (filling it)

TABLE 2.3
Quantitative Analysis by ICP-AES and Ionic Chromatography of the Major Cations and Anions in Mining Water and Solids

Element	Inflow ($\mu\text{g L}^{-1}$)	Outflow ($\mu\text{g L}^{-1}$)	P-deposit (Inflow) (mg kg^{-1})	P'-deposit (Outflow) (mg kg^{-1})
Fe (mg L^{-1})	98.57	34.10	600×10^3	610×10^3
Fe ²⁺ /Fe ³⁺	88.00	22.00	—	—
Cr	2.79	1.98	25.80	82.00
As	47.42	10.61	438.00	460.00
Ba	5.55	12.99	39.00	456.00
Nd	9.14	9.29	18.70	41.23
Ce	32.07	33.85	32.43	95.63
La	13.83	14.33	12.25	38.39
U	561.80	634.00	91.55	213.70
Cu	4.38	7.40	8.80	27.60
Pb	1.23	4.39	12.00	21.40
Zn	107.63	142.00	15.20	88.90
Ni	62.87	75.22	13.70	31.90
Co	44.87	56.51	4.27	17.50
SO ₄ ⁻ (mg L^{-1})	1938.00	1888.0	nd	nd
Cl ⁻ (mg L^{-1})	177.00	157.00	nd	nd
F ⁻ (mg L^{-1})	25.00	24.20	nd	nd

and forms a lake. The seriousness of this problem is demonstrated by the example of Berkeley Pit in Montana (<http://formontana.net/pit.html>), which extends over an area of 77 ha, is 542 m deep, and is filling at a rate of 23 million liters per day [56]. Currently, the water contains approximately 180 mg L^{-1} of Cu and 500 mg L^{-1} of Zn in combination with 1000 mg L^{-1} of Fe, and has an acidic pH of 2.8. This site has also been designated as the experimental site of the US “environmental superfund” for testing metal removal/recovery techniques.

The movement of tailings-derived water away from mining sites and into adjoining surface and groundwater flow system constitutes an ever-increasing environmental problem of truly monumental dimensions. The major problem is that it is difficult, in many instances almost impossible, to contain or curtail AMD. It is the most persistent and, unfortunately in many instances, NONPOINT source pollution problem of mining regions. There is no typical acid mine water, the ferric to ferrous ion ratio may vary, and several other ions such as silica, aluminum, calcium, or magnesium may be present in significant quantities in addition to the dissolved other toxic heavy metals. Untreated AMD pollutes receiving streams and aquifers. The impact on the environment can be severe, leading to a virtual disappearance of aquatic life, a low pH of the water, and a coating of river bottoms with a layer of rust-like particles. Milling operations include the comminution and concentration of the ore. Waste rock and the process water from these operations are usually discharged into large basins called “tailing ponds.” Although most of the heavy metals are present in the form of suspended solids that settle to the bottom of the basins, the overflow from these ponds still contains low but significant concentrations of toxic metals [52]. Furthermore, the dams of these ponds are often constructed from waste rock; thus seepage from the tailings contributes to AMD [53].

2.3.1.3 Radioactive AMD

The uranium mining industry produces a large volume of low-level radioactive waste material, which, following milling, extraction, and neutralization processes, is deposited in extensive tailings

impoundments. As mentioned, in many cases the ore bodies are associated with metal sulfides such as pyrite, marcasite, and pyrrhotite, which are not desired products and are released to the tailings as part of the mill wastes. Upon weathering, these metal sulfides are readily oxidized, producing AMD conditions from these tailings piles, with subsequent leaching of the tailings material resulting in highly acidic pore water containing significant concentrations of iron, sulfate, heavy metals, and trace radionuclides. The migration of such poor-quality tailings water by either surface runoff or subsurface groundwater can lead to serious deterioration in the quality of adjacent natural water systems.

The mining industry is thus faced with the difficult task of devising long-term abandonment schemes that minimize pyrite oxidation and prevent the release of contaminants to the environment. These schemes should be cost effective and should require very little future maintenance or monitoring. Some radionuclides found in water, particularly uranium, thorium, and radium, originate from natural sources, particularly leaching from minerals. The levels of radionuclides found in water typically are measured in units of picoCuries per liter (one picoCurie is equal to 2.2 disintegrations per minute). The US Public Health Service specifications stipulate that water supplies should not contain more than 3 picoCuries per liter of naturally occurring radium-226. The uranium tailings will require proper management technology, without much human involvement in the form of continuous treatment and monitoring, in limiting the release of contaminants to the environment. The mining and milling of uranium-bearing ores results in four types of waste: waste rock, mine water, process effluents, and solid wastes (tailings). Liquid effluents appear to be the most serious waste disposal problem from operating mines and mills, and the chemicals added in the milling process are of particular concern. The solid wastes represent a problem on account of both their magnitude and their radioactivity. On abandonment, the containment of the radioactivity is of utmost concern because of the hazards of long-lived radioisotopes in liquid effluents. A brief list of radioactive elements and their respective half-lives is presented in Table 2.4.

2.3.1.4 Treatment of AMD

The control and prevention of radionuclides and heavy metals contamination of surface and groundwater is best made during the ore treatment procedure and prior to waste and effluent disposal to tailings impoundments. Ideally, due to their persistent nature in the environment and toxicity, the ultimate treatment of heavy metals in effluents would be either their very stable mineralization and deposition, or a complete recovery (and recycle) [57]. However, as these alternatives could hardly be cost feasible and reasonably expected, carefully crafted regulatory limits on the discharge of metals into the environment need to be crafted and adhered to with strict enforcement.

2.3.1.4.1 Lime Addition

Upon disposal of effluent waste to tailings impoundments, lime and barium chloride are added to reduce the acidity and promote the chemical precipitation of heavy metals and radionuclides. However, this treatment mode is a nonpermanent solution because tailings are subject to continuous infiltration by rainfall and an oxygen supply that increases the acidity of water due to sulfide oxidation and promotes the formation of heavy metal and radionuclide leachates. Lime therefore has to be added continuously; thus increasing sludge volumes with time, sludge volumes produced by lime addition will be greater than the tailing waste volumes! This is clearly not the best long-term treatment method to abate AMD.

2.3.1.4.2 Vegetation Cover

The most promising long-term compromise solution has been establishing a vegetation cover directly on the tailings material [58]. The vegetative cover on tailings has provided greater surface stability by controlling erosion and has improved the general aesthetics of the area. Its overall effect on acid generation and tailings area water quality, however, cannot be established to date. There has been no evidence of improvement in the quality of water that leaves a tailings area even though a site may have been vegetated for the last 10 years.

TABLE 2.4
Persistent Radionuclides in Water

Radionuclide half-life reaction, source, comment from reactor, and weapons fission:

Strontium-90	28 years	Fission products	radioisotopes of highest significance
Cesium-131	30 years	because of their high yields	
Iodine-131	8 days	and biological activity	
Cobalt-60	5.25 years	from nonfission neutron reactions	in reactors
Iron-55	2.7 years	$^{56}\text{Fe}(n,2n)^{55}\text{Fe}$,	from high-energy neutrons acting on iron in hardware
Manganese-54	310 days	from nonfission neutron reactions	in reactors
Plutonium-239	24,300 years	$^{238}\text{U}(n,\gamma)^{239}\text{Pu}$,	neutron capture by uranium
Barium-140	13 days	these fission products	
Zirconium-90	65 days	are listed here	
Cerium-141	33 days	in generally decreasing	
Strontium-89	51 days	order of	
Ruthenium-103	40 days	fission yield	
Naturally occurring from ^{238}U series:			
Radium-226	1620 years	diffusion from sediments,	atmosphere
Lead-210	21 years	^{226}Ra —6 steps— ^{210}Pb	
Thorium-230	75,200 years	^{238}U —3 steps— ^{230}Th	produced <i>in situ</i>
Thorium-234	24 days	^{238}U — ^{234}Th	produced <i>in situ</i>

Naturally occurring and from cosmic radiation:

Carbon-14	5730 years	$^{14}\text{N}(n,p)^{14}\text{C}$,*	thermal neutrons from cosmic or nuclear weapon sources reacting with N_2
Silicon-32	300 years	$^{40}\text{Ar}(p,s)^{32}\text{Si}$,	nuclear splitting of the nucleus of atmospheric argon by cosmic-ray protons
Potassium-40	1.4×10^9 years	0.0119%	of natural potassium

2.3.1.4.3 Wet Barriers and Wetlands

Wet barriers, such as water and/or wetland cover on tailings, are believed to be effective in preventing acid generation by cutting off the oxygen supply to the tailings (Nicholson, 1988). The anoxic conditions so produced further support the growth of anaerobic heterotrophes such as sulfate reducers, which, with the breakdown of sulfates, produces hydrogen sulfide, thereby precipitating dissolved metals as sulfides [59]. Wet barriers are therefore artificial whereas wetlands are natural. Analysis of algae from a wetland that was removing manganese from mine water demonstrated phenomenal plant uptake, and Mn concentrations as high as 56,000 ppm (dry weight) were recorded. Iron and manganese oxidizing bacteria are also very active in these acidic wetlands; so much so that some researchers believe they are the most critical aspect of metal removal in cattail marshes [60]. In the organic-rich substrate, other bacteria are active. *Desulfovibrio desulfuricans*, for example, converts the sulfate component of mine water into hydrogen sulfide. This, in turn, reacts with dissolved metals, adsorbed metals, and precipitated metals to form insoluble metal sulfides. This is the eventual fate of all the metals removed from acid water, as dead vegetation sinks to the bottom and is replaced by new vegetation. Absorption by the organic substrate (especially peat) can also be very high. Finally, there are geochemical removal mechanisms occurring in the wetland that may be significant. For example, the cattail marshes that are most successful in removing manganese all have an incorporated layer of limestone beneath the organic substrate. This produces an environment of near-hyeneutral pH and high carbon dioxide concentrations (due to neutralization reactions) and may result in the precipitation of manganese carbonate. Artificial wetlands constructed for the treatment of wastewater or AMD have different design considerations than those for the control of flood, storm, or wildlife habitat management.

Q9

2.3.2 METAL FINISHING AND SURFACE TREATMENT OPERATIONS

Surface finishing consists of various chemical and physical processes, including electroplating, that change the surface of a product or enhance its appearance, increase its corrosion resistance, or produce surface characteristics essential for subsequent operations. The major surface finishing operations consist of pretreatment, electroplating, electroless plating, anodizing, chromating (conversion coating), cyanide hardening, and quenching. The most prevalent surface finishing operations are electroplating, anodizing, and hot dip galvanizing. Table 2.5 gives a breakdown of metal finishing by specific industry.

Surface treatment is applied mainly to metal parts, but also to certain synthetic materials. It involves the following:

- a preliminary preparation of the surface (degreasing and pickling),
- a coating by means of electroplating,
- a coating by chemical means.

Automobile Parts: In recent years the use of electroplated metals for decoration in the automobile industry has fallen drastically. The reasons for this change are a trend toward smaller cars and a designer preference for materials other than nickel and chrome. Bumper manufacturers are the major clients for decorative surface finishing services. Although the trend to soft plastic coatings and paint finishing on bumpers has reduced this market, the demand in the United States for this plating service is larger than the present capacity. Consequently, increased nickel and chrome plating in Canada is expected for the next few years. Demand for functional finishes has increased with pressure to reduce corrosion and extend the life of vehicles. As a result, zinc plating will continue to grow at about 10–20% per year as usage extends to more automobile parts.

Steel Strip Mills: Cold rolled steel in strip form is plated with either zinc or tin. The zinc-plated strip is used in the fabrication of parts that require added corrosion protection on interior surfaces. Tin-plated strips are used primarily in can manufacturing; however, aluminum is replacing tin-plated cans in more and more areas.

Hardware: The demand for hardware products comes directly from the housing and construction industry and the quantity of surface finishing required fluctuates accordingly. The types of surface finishes required are nickel–chrome, zinc, brass, and bronze.

TABLE 2.5
Surface Finishing Market Breakdown

Industry	% of Market (Canada, 1983)
Automobile parts	26.0
Steel strip mills	14.0
Hardware	12.0
Electrical appliances	10.0
Wire goods	10.0
Plumbing fixtures electrical	6.0
Electrical equipment	5.0
Furniture	5.0
Pole hardware and heavy steel	5.0
Electronics	4.0
Engine and worn parts	2.0
Hollowware and flatware	0.5
Jewellery	0.5

Electrical Appliances: The major appliance industry, including manufacturers of stoves and refrigerators, has a constant requirement for surface finishing, primarily for decorative nickel–chrome plating on handles and trim. No increase in the surface finishing demand is expected from this industry.

Wire Goods: These products include display racks, shelving, and shopping carts. The typical surface finish is electroplated nickel, chrome, and brass. Applications for wire goods are numerous and growth potential is in the order of 5–8% per year.

Plumbing Fixtures: These products include taps and bathroom and kitchen fixtures. Base metals are either zinc or chrome plated. Demand is related to the housing and construction industries.

Electrical Equipment: Products included in this group are service boxes, conduit pipes, and transformer parts. Zinc and tin electroplating is used. Surface finishing production rates for these goods fluctuate with the housing and construction industries.

Furniture: Steel furniture is usually plated with nickel and chrome, nickel and brass, or brass only. Growth in this area is highly variable and difficult to predict as it depends on regional trends and designer preference.

Pole Hardware and Heavy Steel: Products such as highway guard rails, transmission towers, and some heavy steel structures used in construction are included here. Hot dip galvanizing is used since the parts are too big to electroplate.

Electronics: The production of printed circuit boards requires primarily copper plating but nickel, gold, tin, and tin–lead processes are also used. While production rates for printed circuit boards are expected to increase over the next few years, the reduction in the surface areas actually plated and the trend to reduced water usage and metal recovery suggest that pollutant generation rates from this industry will not increase.

Engine and Worn Parts: Parts requiring surface finishing come from pumps, diesel engines, gasoline engines, paper mill rolls, etc. The parts vary in size and require heavy deposits of chromium to restore the original dimensions and to provide a durable surface coating.

Hollowware and Flatware: Hollowware products include coffee pots, tea pots, ice bowls, cream and sugar pots, gravy boats, and flower holders. These products are often plated with silver using a silver cyanide bath. There is little growth expected in this market. Flatware includes tableware such as knives, forks, and spoons. These products are made either from stainless steel or from cold-rolled steel, which is plated in a silver cyanide solution. Demand for the product is primarily dependent on the population growth and on the formation of new households; consequently little growth is expected in the future.

Jewellery: All costume jewellery falls under this heading. The typical surface finish is a flash-coating of precious metals such as gold or rhodium on a nickel base. Annual growth is expected to be about 1–3%.

Effluents from a finishing industry must be separated into three categories:

- concentrated spent baths,
- wash waters containing an average concentration of substances likely to precipitate (soaps, greases, and metallic salts),
- dilute rinse water that may be recyclable after treatment.

To secure and facilitate treatment, acidic and chromate-laden effluents must be separated from alkaline and cyanide effluents. The average composition of wastewaters from a surface finishing plant is presented in Table 2.6.

TABLE 2.6
Principal Constituents of Untreated Effluents from Major Metal Finishing Processes.
Composition of Wastewater from Surface Finishing Industries

Species	Plating on Steel	Plating on Zinc	Plating on Brass	Plating on Plastic	Anodizing	Concentration (mg L ⁻¹)
Fe ²⁺	x					1–10
Cu ²⁺	x	x	x	x		5–50
Ni ²⁺	x	x	x	x	x	2–15
Cr ⁶⁺	x	x	x	x	x	10–120
Cr ³⁺	x	x	x	x	x	0.1–1
Zn ²⁺	x	x				10–50
Cd ²⁺	x					10–50
Sn ²⁺	x			x		0.1–20
CN ⁻	x	x	x			1–50
SO ₄ ²⁻	x	x	x	x	x	15–25
Cl ⁻	x	x	x			1–250
CO ₃ ²⁻	x	x	x	x		10–50
Si ₃ ²⁻	x	x	x	x		30–50
PO ₄ ³⁻	x	x	x		x	20–50
Organics	x	x	x	x		0.1–1

Source: Environment Canada, Environmental Protection Service. Overview of the Surface Finishing Industry: Status of the Industry and Measures for Pollution Control. EPS 2/SF/1, Ottawa, Canada, p. 43, 1987.

The pollutants may be divided into several families:

- toxic pollutants such as CN⁻, Cr(VI), and F⁻,
- pollutants that change the pH, that is, acidic or basic substances,
- pollutants that raise the SS level such as hydroxides, carbonates, and phosphates,
- pollutants covered by a particular regulation, S²⁻ and Fe²⁺,
- organic pollutants (EDTA, etc.), especially from degreasing.

All the constituents of baths are found in the rinse water, which may also contain metallic ions (Ni, Cr, Cu, Zn, Sn, Cd, Au, Ag, Pb, Fe, and some others) dissolved from the parts treated. The discharge conditions standards vary greatly, depending on the country, and are rapidly becoming increasingly strict as to pollution concentration as well as the flows of rinse water. A large portion of these effluents is received by municipal sanitary sewers (78%). The heavy metals are generally removed by the activated sludge process and become a part of the resulting biological sludge. The beneficial properties of the sludge, which is often used as a fertilizer in agriculture, are then limited because of the heavy metal content [61].

The general guidelines to limit pollutant discharges from surface finishers depend on the laws of each country. In France, for example (decree of November 8, 1985), the metal concentration of (Zn + Cu + Ni + Al + Fe + Cr + Cd + Pb + Sn) combined should be less than 15 mg L⁻¹. In particular, the thresholds summarized in Table 2.7 should not be exceeded (mg L⁻¹).

The Canadian federal guidelines [62] for metal finishing liquid effluents presented in Table 2.8 provide a baseline standard for water discharges.

A quick comparison of Tables 2.6 through 2.8 shows that the metal concentrations in untreated plating shop effluents may be as much as 120 times higher than those permissible by law. Clearly, untreated metal plating effluent streams may contribute a large amount of metal pollutants to the

TABLE 2.7
France Guidelines for Metal Finishing Liquid Effluents

Cr VI	0.1	Zn	5.0
Cr III	3.0	Fe	5.0
Cd	0.2	Al	5.0
Ni	5.0	Pb	1.0
Cu	2.0	Sn	2.0

environment. For example, chromium is most likely to be found at high concentrations in the effluent streams.

2.3.2.1 A Typical Electroplating Process

Electroplating is the electro-deposition of an adherent metallic coating upon an electrode, which is the workpiece, for the purpose of obtaining a surface with properties or dimensions different from those of the basic metal. These properties may include improvement of appearance, corrosion protection, wear resistance, etc. The operation takes place in aqueous solutions containing the metal ion to be plated. The workpiece is cathodic, and in most instances the metal ion is constantly replenished from an anode containing the metal. A notable exception is chromium where the anode is insoluble and metal ions are replenished by the addition of chromic acid. Electroplating must be preceded by cleaning and activating operations, and a typical sequence of operations involved would be the following:

1. Vapor degrease or soak clean in an emulsion or detergent cleaner.
2. Spray clean in a detergent cleaner.
3. Electroclean in an alkaline cleaner. (The function of electrocleaning is to remove remaining soil and to make the surface chemically active. The operation takes place in an alkaline solution and the work may be anodic or cathodic.)
4. Sulfuric acid dip.
5. Electroplate.
6. Electroclean.
7. Sulfuric acid dip.
8. Second electroplate. Rinsing would follow each process step except 1.

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Surface finishers produce and discharge a variety of waste streams, including process wastewaters, spent process solutions, sludges, and air emissions. For proper plating to occur, the parts must

TABLE 2.8
Federal Guidelines for Metal Finishing Liquid Effluents

Metal	Cu	Zn	Cd	Cr	Ni	TSS
Maximum total concentration (mg L-1)	1.0	2.0	1.5	1.0	2.0	30.0

Source: Environment Canada, Environmental Protection Service. Overview of the Surface Finishing Industry: Status of the Industry and Measures for Pollution Control. EPS 2/SF/1, Ottawa, Canada, p. 43, 1987.

be clean and free of contamination from previous processes. Considerable quantities of raw water are thus used to rinse the parts. Depending on the process for which the rinsing takes place, the wastewater produced may be acidic or alkaline and may contain particular metals or combinations, solvents or cleaning solutions, and/or particulates. Another source of wastewater contamination comes from floor drains. Often, through poor housekeeping, plating solution is allowed to drip as the rack or barrel is passed from tank to tank, and this solution subsequently finds its way into the plant sewer system. Several waste streams, including spent process solutions and sludges, are considered hazardous. Any substance or mixture being discarded is considered hazardous if it is flammable, carcinogenic, toxic, corrosive, and explosive or meets other criteria developed by a (Canadian) federal-provincial working group. Spent process solutions include the following:

- Acidic waste from pickling, etching, bright dipping, and electropolishing.
- Alkaline cleaning baths and electrocleaning baths.
- Solvent degreasing waste.
- Salt bath descaling solution.
- Spent baths themselves when they can no longer be rehabilitated.

The acidic waste contains a high level of dissolved metals, oils, and suspended particles. The large number of different compounds and additives in cleaning solutions often make recovery of metals or chemicals from the spent solutions impractical. Solvent waste contains soil and oily buildup. Spent plating and coating solutions are generated during electroplating, electroless plating, hot dip coating, anodizing, and chemical conversion coating operations. These wastes, and the relating rinse waters, may be acidic or alkaline and may contain hexavalent and trivalent chrome, cyanide, and other toxic compounds.

A number of metal finishing operations leave sludges on the bottoms of plating bath tanks. Large amounts of sludge are also formed during cleaning, painting, and effluent treatment. Sludge from effluent treatment is only 1–5% solids and can be dewatered to reduce its volume. Sludges usually contain hazardous materials, which could upset the municipal treatment plant if discharged to sewer. Figure 2.9 shows a schematic flow sheet of a copper–nickel–chrome plating system without waste treatment. One should note the numerous opportunities that the wastewater has to pick up pollutants.

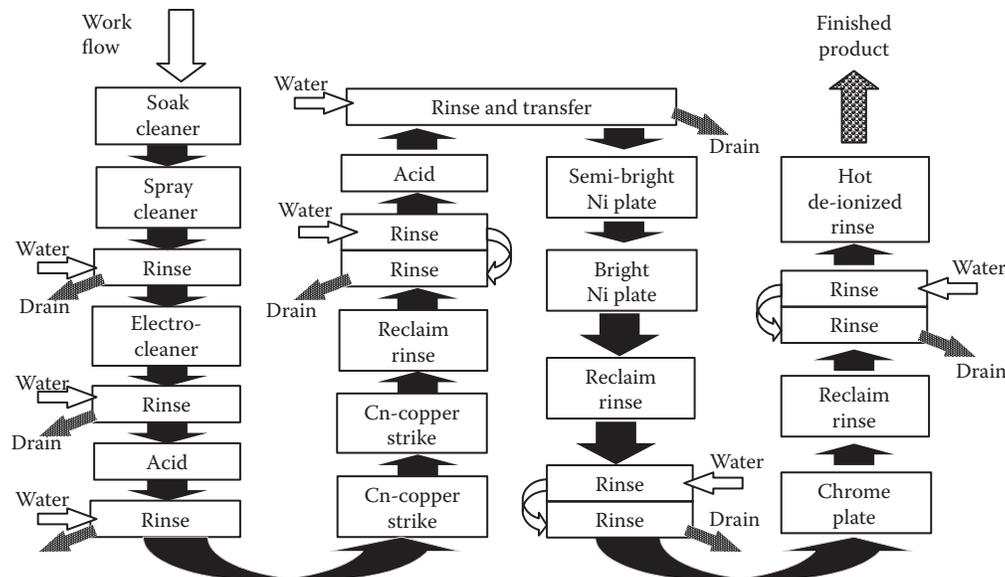


FIGURE 2.9 A schematic flow sheet of a copper–nickel–chrome plating system without waste treatment.

2.3.2.2 Future Trends in Electroplating

Since pressures to reduce impact and liability will continue, if not increase, for the foreseeable future, prudent firms that expect to be using conventional processes are working toward optimizing them. Two popular trends include:

- Approaching zero exposure—isolating employees from contact with materials or effluents in process operations, thus approaching zero risk conditions.
- Approaching zero discharge—maximizing material utilization and recovery, thus minimizing the impact on the environment from wastewater, air emissions, and concentrated waste streams (spent process solutions and treatment sludges and solids).

The techniques that firms employ to achieve near-zero exposure and discharge from wet processes depend on the specific process and production situation, but can involve:

- Enclosing process lines (a common practice in the printed wiring board and semiconductor industries).
- Reducing and recovering dragout.
- Using process solution and rinse purification and recycle technologies.
- Using racking and fixturing off-line to reduce operator exposure and using configurations that optimize process efficiency and yield and minimize waste.
- Using process automation and control systems to optimize material usage and yield.
- Modeling processes for optimization.

Examples of processes using metals with environmental health and safety (EH&S) concerns that can approach near-zero discharge include:

- Chromium plating.
- Chromic anodizing.
- Nickel plating.
- Electroless nickel plating.
- Cadmium plating.
- Lead plating.
- Tin–lead plating.

Hundreds of surface finishing facilities have already implemented process optimization projects that have resulted in near-zero discharge. The improvements have typically yielded cost savings, since the optimized processes exhibit better performance, along with lower material usage and reduced waste generation. In addition, a small fraction of existing surface finishing facilities have enclosed automated process lines with ventilation and air emissions control systems that provide near-zero exposure risk. Industries such as printed wiring board manufacture provide examples where such systems have been successfully implemented.

2.3.3 LEATHER TANNING PROCESS

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep, and pigs. Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used are trivalent chromium and vegetable tannins extracted from specific tree barks. Alum, syntans

(man-made chemicals), formaldehyde, glutaraldehyde, and heavy oils are other tanning agents. The process of leather tanning generates wastewater effluents containing chromium, which, when emitted at high concentrations, can be toxic to the environment. The public's awareness of the dangers of harmful effluents has grown during the past decade and the need for stricter environmental regulations has forced many process-related industries to dramatically refine their dangerous polluting effluents. The industry's growth in the Western world has stagnated since the 1980s due to the influence of more affordable synthetic leather substitutes. Western regulations regarding wastewater controls are more stringent than those of developing countries and this translates into higher relative production costs for the tanners in developed countries.

2.3.3.1 Description of the Chromium Tanning Process

The modern process of chrome tanning dates back to its discovery by Federick Knapp in 1958. The purpose of chrome tanning is to transform a hide or skin into a finished leather product that is insusceptible to putrefaction. By varying the specifics of a process, it is possible to obtain leather with the required grain, temper, break, and strength. Specifically, tanning is the reaction of the collagen protein fibers of the hide with chromium. The most widely believed mechanism is that of a coordination of the protein carboxyl groups with a chromium complex [63]. The tanning process can be divided into three divisions:

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1. **Beamhouse:** Hides are first trimmed and soaked to remove salt and other solids and to restore moisture lost during curing. After soaking, the hides are fleshed to remove excess tissue, to impart uniform thickness, and to remove muscles or fat adhering to the hide. Hides are then dehaired to ensure that the grain is clean and the hair follicles are free of hair roots. Liming is the most common method of hair removal, but thermal, oxidative, and chemical methods also exist. The normal procedure for liming is to use a series of pits or drums containing lime liquors (calcium hydroxide) and sharpening agents. Following liming, the hides are dehaired by scraping or by machine. Deliming is then performed to make the skins receptive to vegetable tanning, which is a long-drawn process (~3 weeks) starting with low chemicals concentration that is gradually increased as tanning proceeds.
2. **Tanyard:** Chrome-tanned leather tends to be softer and more pliable, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. Almost all leather that is made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned. The first steps of the process (soaking, fleshing, liming/dehairing, deliming, bating, and pickling) and the drying/finishing steps are essentially the same as in vegetable tanning. However, in chrome tanning, the additional processes of retanning, dyeing, and fat liquoring are usually performed to produce usable leathers, and a preliminary degreasing step may be necessary when using animal skins, such as sheepskin.

Chrome tanning in the United States is performed using a one-bath process that is based on the reaction between the hide and a trivalent chromium salt, usually a basic chromium sulfate. In the typical one-bath process, the hides are in a pickled state at a pH of 3 or lower, the chrome tanning materials are introduced, and the pH is raised. Following tanning, the chrome-tanned leather is piled down, wrung, and graded for thickness and quality, split into flesh and grain layers, and shaved to the desired thickness. Grain leathers from the shaving machine are then separated for retanning, dyeing, and fat liquoring. Leather that is not subject to scuffs and scratches can be dyed on the surface only. For other types of leather (i.e., shoe leather), the dye must penetrate further into the leather. Typical dyestuffs are aniline-based compounds that combine with the skin to form an insoluble compound.

Fat liquoring is the process of introducing oil into the skin before the leather is dried to replace the natural oils lost in beamhouse and tanyard processes. Fat liquoring is usually performed in a

drum using an oil emulsion at temperatures of about 60–66°C (140–150°F) for 30–40 min. After fat liquoring, the leather is wrung, set out, dried, and finished. The finishing process refers to all the steps that are carried out after drying. Chromium (trivalent) tanning agents are added in the tanning step. Any unfixed tanning agents are removed from the leather in the wringer. The products at this point are referred to as blue hides. Tanneries often perform only the beamhouse and tanyard processes and sell their “blue” hides to retanners.

2.3.3.1.1 Beamhouse Operations

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Cured hides received from market must undergo pretreatment before they can be processed into leather. The objective of beamhouse operations is to prepare the hides. Figure 2.10 shows a schematic for the process. In the side-and-trim step the hides are cut into two sides and any unwanted sections of the hide are trimmed off. The wash-and-soak step involves soaking of the hide in water for 8–20 h. The hides absorb water to make up for the moisture lost in the curing process. Washing removes nonfibrous proteins, dirt, salt, blood, and manure from the hide. Fleshing is the mechanical removal of excess flesh, fat, and muscle from the hide. This is done in cold water so as to ensure that the fat remains congealed. Alkaline chemicals (Na_2S and NaOH) are then added to dissolve any hair and to destroy hair roots.

2.3.3.1.2 Tanyard Process

A schematic for the tanyard process is shown in Figure 2.11. Sulfated/chlorinated ammonium salts are added in the bating step to solubilize any alkaline material present from the beamhouse process. Bates (enzymes) are added to further destroy hair roots and pigments and to prepare the collagen fibers for their reaction with the tanning agents. An acidic medium is required for chrome tanning; hence the addition of H_2SO_4 in the pickling step ensures that all alkaline material has been washed away. Salt is also added in the pickling step as it prevents “acid swelling” by reducing excess moisture. Chromium (trivalent) tanning agents are added in the tanning step. Any unfixed

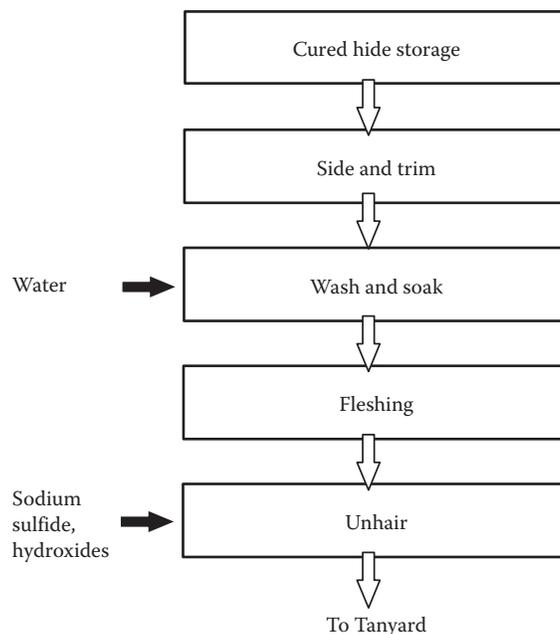


FIGURE 2.10 Leather tanning—a box schematic diagram for the beamhouse process.

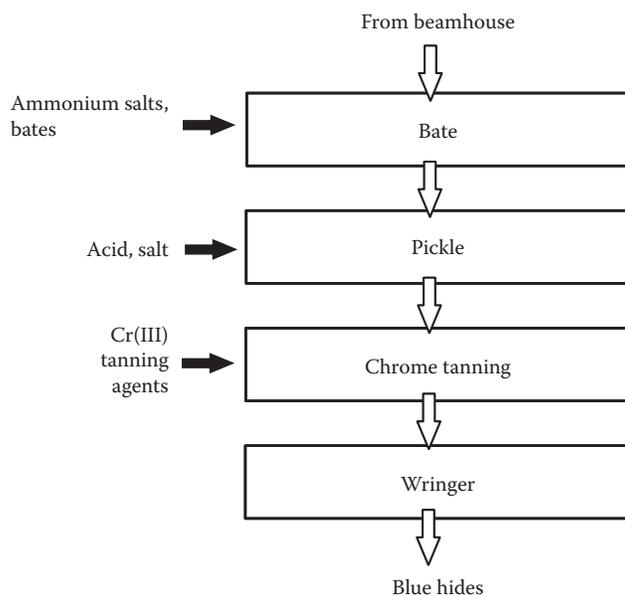


FIGURE 2.11 Leather tanning—a box schematic diagram for the tanyard process.

tanning agents are removed from the leather in the wringer. The products at this point are referred to as blue hides.

2.3.3.1.3 Retanning

Retanning is necessary to convert the blue hides to leathers suited for a specific use. A schematic for the process is shown in Figure 2.12. Chromium is usually used as the retanning agent. The leather quality is often upgraded by the introduction of phenols and other complementary tanning agents. The leather is then bleached and dyed as desired. The addition of fat liquor replaces any natural oils lost in the beamhouse and tanyard processes. Final finishing includes drying, conditioning, buffing, and plating.

2.3.3.2 Wastes Generated in the Chromium Tanning Process

The beamhouse process normally accounts for about 40% of wastewater volume in a tannery [64]. Beamhouse wastes have a high pH of 10–12 and contain high amounts of proteins and sulfides. Nitrogen, BOD, and TSS are also very prevalent in beamhouse wastes. Wastes from the bating step have high ammonia concentrations and also contain proteins and dissolved hair. The pickling step generates a highly acidic waste (pH 2.5–3.5) containing salts. Toxic levels of trivalent chromium at elevated temperatures characterize the acidic waste from the tanning and retaining steps. The retanning process also yields wastes containing dyes and sulfonated oils at elevated temperatures. Tanyard and retanning effluents have considerably high levels of COD. These elevated COD levels are caused by high ammonia concentrations from the bating step. In addition to nitrogenous COD demand, if a phenol retanning step is used in the process it may account for up to 30% of the total COD [65]. The retanning finishing step also contributes to higher levels of COD. This is due to the introduction of organic dyes, sulfonated oils, pigments, and coatings.

2.3.3.2.1 A Leather Tannery Wastewater Case

Production levels, seasonal variations, process variations, and the batch nature of tannery operations result in large variations in the wastewater sampled parameters. A medium-sized tannery

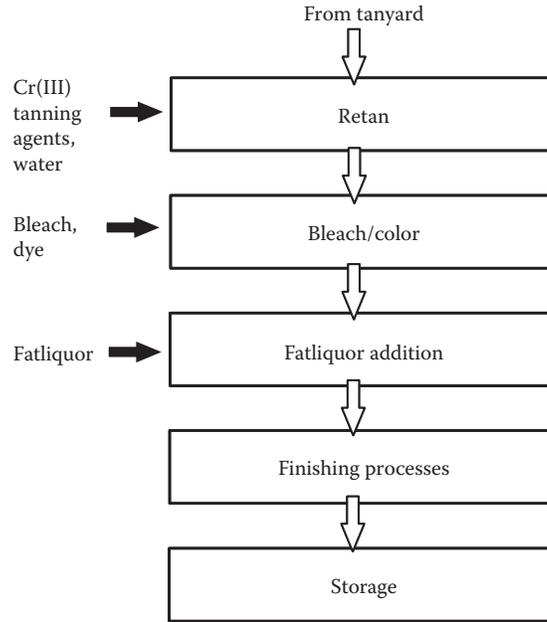


FIGURE 2.12 Leather tanning—a box schematic diagram for the retanning process.

may typically process 500–1000 kg of hides in one batch. About 50,000–150 L of water are used for each batch, thus requiring approximately 200,000–500,000 L of water per day. Table 2.9 shows a typical case raw effluent composition.

It is evident from the above table that extremely high chromium concentrations are present. This is due to the washing of the chromium from the original tanning step. It can be seen that high concentrations of undesirables are present. Table 2.10 shows the parameters for river outfall. High levels of chromium, phenols, COD, BOD, and oil and greases are present following a simple settling pretreatment. The highly acidic nature of the effluent (pH 3.3) should be raised to a more moderate level. High levels of COD exert a heavy load on the receiving water body and require a special treatment to reduce them. The case is similar for chromium content.

TABLE 2.9
Original Wash Sampling Results* (pH 5.0)

Parameters	#1	#2	#3
Total solids	5444	—	2520
TFS	1480	140	127
Oil and grease	0.42	88.5	94.7
BOD	536	120	410
COD	3047	1445	1032
Pb	1.1	7.5	7.5
Cr	122	140	120
Phenols	0.14	2.5	1.95

Note: *All results are in mg L⁻¹ (ppm).

TABLE 2.10
River Outfall Sampling Results* (pH 3.3)

Parameters	#1	#2	#3
Total solids	1540	—	1300
TFS	—	88	165
Oil and grease	0.01	44	98.7
BOD	454	238	904
COD	2500	1875	3016
Phosphates	0.25	3.7	—
Pb	0.25	7.75	7.5
Cr	91	40	130
Phenols	0.52	1.55	0.40
NH ₄	—	0.91	1.61

Note: *All results are in mg L⁻¹ (ppm).

2.3.3.3 Effluent Treatment

There are various options for reducing chromium effluent concentration in a leather tanning process. Chrome recycling within the process can account for large economic savings with respect to the amount of chemicals required and will allow for a lesser concentrated chromium effluent. Ideally, direct recycling could account for reductions of 40% in “suspended” solids, of 50% in BOD, and of 80% in toxicity [65].

2.3.3.3.1 Changing Process Chemicals

The following are three forms of chemical changes capable of improving effluent quality: organic acid pickling, “low-use” chrome compounds, and synthetic tanning agents. As mentioned in the above description of the chromium tanning process, the pickling step usually employs sulfuric acid to prepare the hides for chrome tanning. Substitution of H₂SO₄ for organic acids can substantially reduce (approximately 20%) the chrome required in the tanning process. Organic acids show a reduced affinity for collagen fibers, thus enabling acid penetration and chrome fixation to occur more rapidly [65]. Employing low-chrome compounds is the most widely used method for chromium effluent reduction. These low-chrome compounds are commercial tanning agents (e.g., Chromotan, Blancoral, and Baychrome 2403) capable of producing quality tanned leather at lower chrome concentrations. Low-chrome compounds combined with low float (liquor to hide ratio) techniques are capable of lowering chrome and water consumption [65]. Substitution of chromium tanning complexes for synthetic tannins would totally eliminate chromium from the process. However, this is not possible because product quality would suffer. The most common of the new synthetic tannins are those of complex aluminum salts. Research is presently being done to find new chrome-free tanning agents consistent with a fine quality of leather [65].

For example, a leather tanning process has been developed in which animal skins are treated with a tanning agent comprising a mixed complex of aluminum(III) ions and titanium(IV) ions, and as a masking compound a salt of a polyhydroxymonocarboxylic acid. Titanyl sulfate solution, prepared by the dissolution of hydrous titanium oxide in sulfuric acid, can be mixed with aluminum sulfate in the desired proportions, treated with masking agent and basified to the appropriate acidity, and then used in the “cleaner” tanning process.

2.3.3.3.2 Treatment Improvements

Process effluent streams containing alkaline materials are segregated from acid streams (containing chromium). High sulfide concentrations in the alkaline streams are first targeted by screening and

then by sulfide oxidation. The oxidation takes place in an aerated tank and uses manganese sulfate as a catalyst. Oxidation may also be forced using peroxide addition. The effluent from the oxidation step is mixed with the segregated acid effluent in an equalization tank. Chromium precipitation and subsequent recycling is another means of reducing chromium in the effluent. This is done by raising the pH to an optimum level (8.5) using a hydroxide. The chromium precipitates as chromium hydroxide ($\text{Cr}(\text{OH})_3$). Coagulants and flocculants are also added to aid in substrate removal. The hydroxide precipitate is then filtered and redissolved in sulfuric acid to form chrome sulfate, which is subsequently recycled [65]. Application of ion exchange resins to remove undesirable ions from wastewater (i.e., chromium) has to be carefully considered in combination with appropriate pretreatment since the organic components in wastewater can seriously affect resin performance. Metal biosorption metal removal/recovery effluent treatment alternative deserves special attention because of the low cost of biosorbent materials. The introduction of newer technologies in both leather tanning processes and the treatment of wastewater can greatly lower the pollution load normally posed by conventional tannery effluent disposal.

2.3.4 FERROUS METAL INDUSTRIES

The production of metals via extraction from metal ores is one of the oldest metallurgical processes. In the Roman Empire, metal production was used to make dishes, tools, and weapons. During the following centuries, more metal was required as a result of industrialization, and the metallurgical industry was born. The modern metallurgical industry can be separated into two main categories: ferrous and nonferrous. Ferrous metallurgy deals with the production of iron and its alloys, whereas nonferrous metallurgy deals with the production of other metals such as copper, nickel, lead, and zinc. Previously, there has been little concern about heavy metal emissions from the industry, owing to ignorance of the impact of heavy metals on the environment. Today, the toxicity of heavy metals is relatively well established and key pollution regulations have been legislated for the mining and metal production industries. Studies have demonstrated that the heavy metal pollution arising from metal production usually becomes water pollution. For example, heavy metals in air emissions are brought down into water during rainfall, they are leached from solids into surface streams and rivers, and effluents from industries are often discharged directly into rivers or other receiving surface water bodies (Figure 2.13).

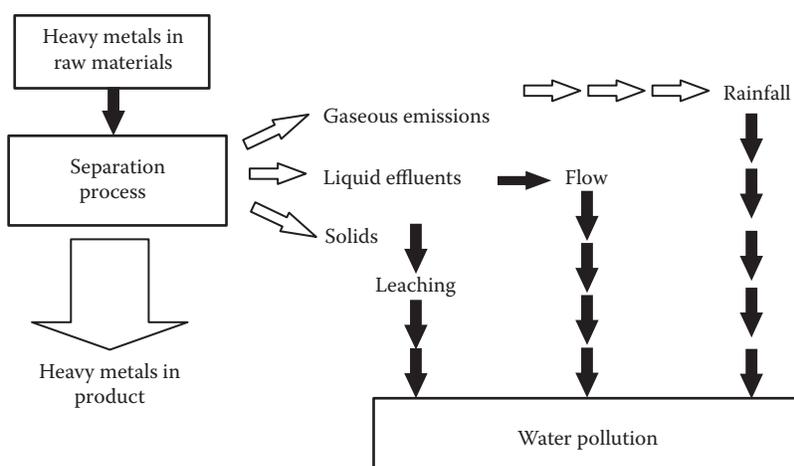


FIGURE 2.13 Heavy metal sources from metal production.

2.3.4.1 Ferrous Metal Processing

Ferrous metal processing can be divided into three categories:

1. Primary iron and steel production.
2. Ferroalloy production.
3. Ferrous foundry production.

The process used in the production of ferrous metals is similar for all three types of production categories and can be summarized in general as illustrated by the flow sheet in Figure 2.14.

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Depending on the category of industry, the furnace and the reactants involve change. Air emissions arise from the recuperation of heavy metals that are in exhausted gas. The recovery is not 100% effective; hence heavy metals are discharged into the atmosphere. The air pollution control equipment used will be different, depending on the type of furnace used. Solid wastes from ferrous processing industries are present in the form of slags and dusts. Dusts that cannot be recycled back into the process are disposed of continuously. Slag comprises waste oxides and is usually dumped in a slag dump. Generally, water pollution comes from process water, contact cooling water, and wash-down water. A sludge plant is commonly used to treat process wastewater. Table 2.11 shows the most common heavy metals that can be found in wastewaters from the three different ferrous industries.

2.3.4.1.1 Primary Iron and Steel Production

Iron is produced by a blast furnace process. Steel is produced from pig iron originating from the blast furnace [66]. In 1976, the Canadian production of steel amounted to 10,916,929 tons from basic oxygen and open hearth furnaces and 1,665,880 tons from electric arc furnaces [66]. Usually, iron and steel production is integrated in the same plant. Total emissions from primary iron and steel production are estimated at 83 tons per year of copper and 51 tons per year of nickel [66]. Heavy metals pollution results from three kinds of emission: water, air, and solids. Table 2.12 gives a comparison between water pollution, air emissions, and solid disposals from an iron and steel

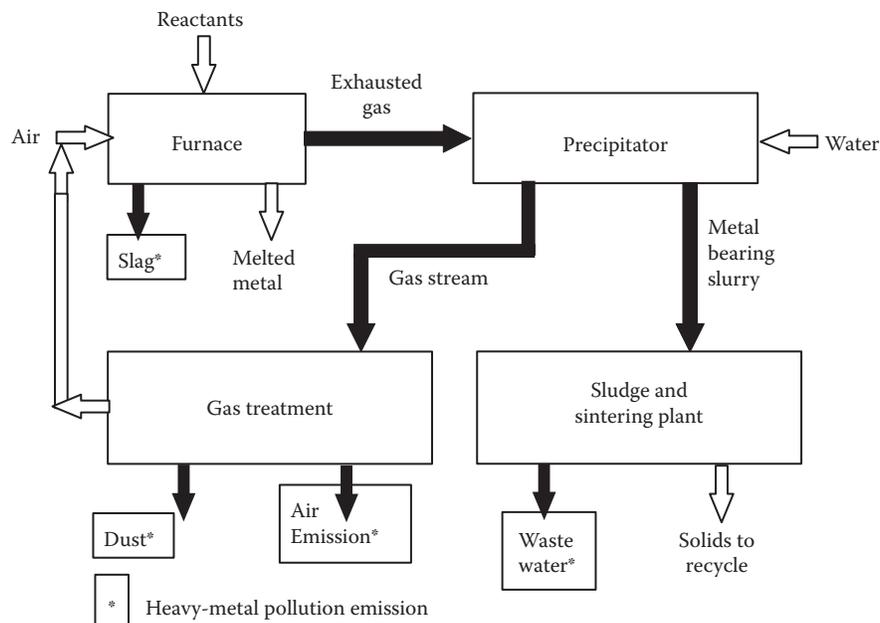


FIGURE 2.14 Flow sheet of a typical ferrous metal production plant.

TABLE 2.11**Heavy Metals in Wastewater from Ferrous Industries**

	Sb	Bi	Cd	Cr	Co	Cu	Fe	Pb	Mn	Hg	Mo	Ni	Se	Zn
Primary Iron	—	—	x	x	x	x	x	x	—	x	—	x	—	x
Ferro-alloy	—	—	x	x	—	x	x	x	—	x	—	x	—	x
Foundries	x	x	x	x	x	x	x	x	x	x	x	x	x	—

making plant. From this table it can be seen that solid disposals are more polluting than water discharges.

2.3.4.1.2 Ferroalloy and Ferrous Foundry Production

A ferroalloy is an alloy consisting of iron and one or more other metals. Various kinds are produced in the world, mainly ferrosilicon, ferromanganese, silicomanganese, and ferrochromium. Table 2.13 shows the composition of the effluent of a ferrochrome production plant.

Foundries range in size from small operations to the large production type, which turn out tonnage casting. Some plants produce special wear- and heat-resistant castings, which are usually high alloy. Other plants produce the normal gray iron and ductile iron castings, which may weigh from a few ounces to several tons. Because of the various operation conditions (capacity and charge), no typical data have been found that could be considered as representative of the industry branch.

In conclusion, in ferrous metal production, solid wastes contain the highest amounts of heavy metals followed by air emissions and liquid effluents. Solid wastes are considered as relatively inert. The air emission and liquid effluents containing heavy metals are the most damaging to the environment, since these heavy metal concentrations and discharge rates are very high and can be easily brought into the water table or accumulate directly in the aquatic environment and biota.

2.3.5 COAL-FIRED POWER GENERATION

The whole thermal-power industrial sector, including both conventional and nuclear power generating plants, withdrew 64% of the total water intake in 1996. Next to fuels, water is the most important resource used in large-scale thermal power production. The production of 1 kw h of electricity requires 140 L of water for fossil fuel plants and 205 L for nuclear power plants. Some of the water

TABLE 2.12
Amount of Wastewater, Air Emissions, and Solid Disposals for an Example of an Iron Making Plant

Pollutant	Wastewater Effluents (kg h ⁻¹)	Air Emissions (kg h ⁻¹)	Solid Disposals (kg h ⁻¹)
Cd	<0.023	—	—
Cr	<0.023	—	3
Cu	<0.023	1	7
Fe	0.517	—	422
Pb	<0.025	7.23	62
Mn	—	2.71	36
Ni	<0.023	0.41	—
Zn	<0.025	—	160

TABLE 2.13
Concentrations of Metals in Effluents from a Ferrochrome Production Plant

Pollutant	Stream #1 (mg L ⁻¹)	Stream #2 (mg L ⁻¹)	Stream #3 (mg L ⁻¹)
Fe	<0.1	<0.1	0.3
Cr	<0.1	<0.1	<0.1
Cu	<0.01	0.02	<0.01
Pb	<0.11	<0.1	<0.1
Mg	24	59	1.5
Hg	<0.0005	<0.0005	<0.0005
Cd	0.019	<0.005	<0.005
Zn	61	0.3	0.02
Ni	0.06	0.01	<0.05

is converted to steam, which drives the generator producing the electricity. Most of the water, however, is used for condenser cooling because today's processes can only convert 40% of the fuel's energy into usable electricity. The rest is wasted. This shows the double cost of inefficient energy use: first, in the wasted energy, and then in the water required to cool the wasted heat to the temperature where it can be released safely into the environment. This requires a continuous flow of cooling water circulating through the condenser. All the cooling water is therefore returned to the environment much warmer. However, the temperature can be reduced using cooling towers and other such devices.

Nonnuclear thermal electric power generating stations are a somewhat less known source of a large amount of metal emissions yearly. This is due to the large flowrates of water involved in operation of the plants. On the other hand, their consumption of coal that brings in trace metal impurities is truly gigantic. A large coal train called a "unit train" may be 2 km (over a mile) long, containing 100 cars with 100 tons of coal in each one, for a total load of 10,000 tons. A large plant under full load requires at least one coal delivery this size every day. Plants may receive as many as three to five trains a day, especially in "peak season," during the summer months when power consumption is high. A large thermal power plant (e.g., Nanticoke, Ontario, Canada) could store several million tons of coal for winter use when the supply faces interruptions.

Metals from coal, as they do not combust, end up in their gaseous, aqueous, and solid waste streams. Coal also contains low levels of uranium, thorium, and other naturally occurring radioactive isotopes whose release into the environment leads to radioactive contamination. While these substances are present as very small trace impurities, enough coal is burned that significant amounts of these substances are released. A 1000 MW coal-burning power plant could release as much as 5.2 tons per year of uranium (containing 74 pounds of uranium-235) and 12.8 tons per year of thorium. The radioactive emission from this coal power plant is 100 times greater than a comparable nuclear power plant with the same electrical output; including processing output, the coal power plant radiation output is over 3 times greater [67].

Trace amounts of mercury exist in coal and other fossil fuels [68]. When these fuels burn, toxic mercury is released, which accumulates in the food chain and is especially harmful to aquatic ecosystems. Worldwide emissions of mercury from both natural and human sources were estimated at 5500 tons in 1995 [68]. US coal-fired plants emit an estimated 48 tons annually, which is approximately one-third of all mercury emitted into the air by human activity in the USA [68]. In contrast, China's coal-fired power plants emitted an estimated 68 tons of mercury in 1999, which was about one-eighth of Chinese human-generated mercury emissions [69].

Of the three types of plants (coal fuelled, oil fuelled, and mixed), coal-fuelled plants are the worst polluters due to the high-sulfur coal burned and their high water consumption rates. It is possible to significantly reduce metal emissions if appropriate and currently available technologies are incorporated

into the power generation operation schemes. Unfortunately, too few plants have made any efforts to address this particular problem, which remains as overwhelming as ever.

2.3.5.1 Coal-Fired Station Types

There are two types of generic station types. The waste stream compositions of each model depend on coal composition, scrubber design, and system operation. For instance, the “Eastern” type of power plant uses high-sulfur bituminous coal fuel, while the “Western” type uses low-sulfur lignite coal fuel. Unfortunately, available sources list only the emission of iron from streams, specifically, grouping all other metals present into one category. The other metals that may be present are aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, thorium, titanium, vanadium, zinc, and zirconium. However, the metals usually present in the largest concentrations are aluminum, manganese, iron, nickel, copper, zinc, and vanadium [70].

First Model (Eastern) – Typical Characteristics:

- 400 MW generating capacity,
- high-sulfur bituminous coal fuel,
- dry fly ash handling system,
- recirculating bottom ash handling system,
- once-through seawater cooling,
- limestone-based flue gas desulfurization,
- combined fly and bottom ash disposal area,
- separate flue gas desulfurization (FGD) sludge disposal area.

Periodic wastewater streams contain metals from the substances removed during the annual boiler and equipment cleaning. These streams are high in metal concentrations (Table 2.14). Some

TABLE 2.14
First Model (Eastern) of a Power Generating Station—Stream Data

Source	Flow (L y ⁻¹)	Iron (mg L ⁻¹)	Other Metals (mg L ⁻¹)
Periodic:			
Air preheater wash	500,000	7560	1320
Boiler fireside wash	1,000,000	1060	935
Boiler steamside wash	600,000	6900	1000
Continuous:			
	L s⁻¹		
Coal pile runoff	0.6	5320	610
Filter backwash	0.9	0.7	5.2
Ionex regeneration	1.3		
Cation		0.3	7.1
Anion		6.2	0.5
Fly/bottom ash disposal	1.5	0.7	17
Bottom ash blowdown	23	23	20
Boiler room sump	20	13	60
Condensate polisher	0.4	0.2	<0.1
Cooling water	17,000	1.1	7.5
FGD sludge disposal	1.5	0.4	20
FGD system blowdown	11	1.0	14

Source: Environment Canada, Environmental Protection Service. *Significance and Treatment of Dissolved Solids in Wastewaters from Canadian Steam Electric Stations*. Ottawa, ON, Canada, 1985.

continuous wastewater streams contain high metal concentrations. These are produced in the daily operation of the station from the condenser cooling blowdown, the ash transport systems, and FGD systems. While metal concentrations in other continuous streams may be relatively low, from 1–10 mg L⁻¹, some of these streams have very large flowrates [70].

Periodic wastewater streams annually emit 8980 kg of iron and 2195 kg of other metals. Continuous streams emit 715,957 kg y⁻¹ of iron and 4,091,957 kg y⁻¹ of other metals. This is an annual total of almost 5 million kilograms per year of metals emitted into the environment.

Second Model (Western) – Typical Characteristics:

- 400 MW generating capacity,
- low-sulfur lignite coal fuel,
- combined fly and bottom ash transport with lagoon disposal,
- recirculating cooling tower,
- no FGD.

The western stations tend to be more modern and to employ more advanced technology, particularly in the cleaning of streams. Unfortunately, no general composition data are readily available for periodic wastewater streams. Continuous wastewater discharge streams show a significant reduction in metal concentrations due to the use of lower-sulfur coal and the presence of cooling towers that reduce the water flows (Table 2.15). With the cooling towers, less fresh water is used and greater concentrations of metals can be removed before emission. Unfortunately, there is still the blowdown water, which is taken from the recirculating water to control the buildup of suspended and dissolved solids in the system.

The annual amount of iron released into the environment from continuous streams is 22,889 kg; the amount of other metals is 94,027 kg. This is a reduction of 96.8% and 97.7%, respectively. The majority of this reduction is due to the use of cooling towers and more efficient cleaning prior to emission through the use of reverse osmosis [70].

TABLE 2.15
Second Model of a Power Generating Station—Stream Data

Source	Flow (L y ⁻¹)	Iron (mg L ⁻¹)	Other Metals (mg L ⁻¹)
Periodic:			
Air preheater wash	730,000		
Boiler fireside wash	600,000		
Boiler steamside wash	500,000		
Continuous:			
	L s⁻¹		
Coal pile runoff	0.3	530	1670
Filter backwash	0.9	0.7	5.2
Ionex regeneration	3.4		
Cation		0.3	7.1
Anion		6.2	0.5
Combined ash lagoon overflow	30	0.4	15
Boiler room sump	20	1.6	
Condensate polisher	0.4	0.2	0.1
Reverse osmosis reject brine	1.5		
Cooling tower blowdown	100	5	40

Source: Environment Canada, Environmental Protection Service. *Significance and Treatment of Dissolved Solids in Wastewaters from Canadian Steam Electric Stations*. Ottawa, ON, Canada, 1985.

TABLE 2.16
Environment Canada Criteria for Discharge of Wastewaters
from Thermal Power Generating Stations

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Parameter	Acceptable Limits
pH	6.0–9.5
Total suspended solids	25.0 mg L ⁻¹
Chromium	0.5 mg L ⁻¹
Copper	0.5 mg L ⁻¹
Iron	1.0 mg L ⁻¹
Nickel	0.5 mg L ⁻¹
Zinc (system without recycle)	0.5 mg L ⁻¹
Zinc (system with recycle)	0.2 mg L ⁻¹

2.3.5.2 Generating Station Water Use

The steam electric power generating industry is one of the major point-source users of surface waters. Earlier, water was used on a once-through basis for each subsystem of the plant. However, with increased competition for available clean surface water, new designs had to be implemented for plants to reduce water intake. Plants were to maximize the internal reuse of service water streams through recirculation. With lower volumes of wastewater to treat, removal of contaminants could be maximized. Metals in the water streams cause corrosion and scale problems. Most water intake requirements are for major condenser cooling. Water is also used for cooling auxiliary equipment, as boiler makeup water, and for cleaning boilers and other equipment. Particularly in coal-fired plants, water is necessary for coal spray and for the removal and transportation of combustion wastes. The metals present in station effluents, many exceeding environmental guidelines, come from demineralization of water, corrosion of equipment and scaling as well as coal pile runoff—a large source of dissolved metals—and from the cleaning of flue gas through desulfurization (FGD) or the removal of fly ash solids [70]. The various major wastewater streams in the power-generating plant are given below.

TABLE 2.17
Composition of Specific Metal Concentration Present in Station Waste
Stream Versus in Nature

Q15

Parameter	Natural Concentration (mg L ⁻¹)	Waste Concentration (mg L ⁻¹)
Aluminum	0.08	7.4
Manganese	0.05	15.0
Iron	0.047	1300
Nickel	0.005	55
Copper	0.003	8.6
Zinc	0.001	4.3
Barium	0.10	7.9
Vanadium		20.0

Source: Environment Canada, Environmental Protection Service. *Significance and Treatment of Dissolved Solids in Wastewaters from Canadian Steam Electric Stations*. Ottawa, ON, Canada, 1985.

Boiler blowdown: Impurities entering the steam generating system with boiler makeup water and corrosion prevention chemicals are concentrated as steam in the boiler. To avoid excessive buildup of the impurities, the boiler side is bled as a boiler blowdown stream. The boiler blowdown water is discharged over ash dykes.

Demineralization (DM) plant neutralization effluent: Raw water from the clarifier is treated in the DM plant with the help of ion exchange resin beds. During regeneration and backwashing, effluents are generated, which are collected in a neutralization pit. Effluents during regeneration of anionic and cationic beds are mixed together along with other effluents and discharged after pH adjustment into ash ponds. The DM plant neutralization effluent may also be eventually discharged into ash ponds, where it is treated along with other effluents before its discharge into the environment (ash pond overflow).

Cooling tower blowdown: In this system, hot water from the condenser is cooled in the cooling tower and the cooled water is recirculated to the condenser by CW pumps through the water conductor system. The blowdown from the cooling water system is taken to an ash water sump to meet the requirement of the ash handling plant.

Ash pond overflow waters: The ash slurry from the generating units is dumped in the ash dyke area. This area consists of two compartments; the first one consists of 80% of the area where most of the ash is settled and water with fine ash flows into the second compartment (stilling pond). In the stilling pond, final ash is settled. The water from the stilling pond is partially recycled and partially discharged in an open lined channel for irrigation after proper treatment.

Oxidation pond outlet: The wastewater from residential colonies along with sewage generated at thermal plants is led to the oxidation plants. The treated water from the oxidation ponds may be used for irrigation and green belt development.

Collected coal-heap runoff: The mixed runoff generated in the coal-heap area originates from atmospheric deposition (rain and snowmelt), washing, and mainly from coal-heap spraying (to minimize dust and also self-ignition). Due to the action of acid-generating microorganisms, the runoff tends to be acidic (like AMD), effectively leaching trace metal content of the huge quantities of coal throughput. The combined collected runoff of low pH is usually neutralized (lime) and the resulting precipitates settled out as toxic sludge. The water effluent may be discharged or recycled, if feasible. Its residual overall amount of toxic heavy metals in this stream, however, can be quite significant.

2.3.5.3 Conclusions

Thermal stations using fossil fuels have always been linked in the public mind with heavy air pollution. The liquid effluents from these plants have never been given much attention; hence the public has been left with a false sense of security about the purity of the water around thermal power generating plants. However, it is clear that the waste streams being emitted could use much cleaning. Many plants in North America exceed the regulatory norms for concentration of heavy metals in the environment. Unfortunately, those norms are deceptive since the environmental impact of heavy metals is measured more in terms of quantities of metals in the water bodies rather than effluent concentrations. With the immense amounts of water discharged by those plants, even if they met the norms they would still have a considerable impact on nature. A better solution would be to make plants comply with a set amount of metal emissions per day rather than with a specific stream concentration.

REFERENCES

1. Volesky, B., Sears, M., Neufeld, R.J., and Tsezos, M. Recovery of strategic elements by biosorption. In: *Biochemical Engineering 3, Annals NY Acad. Sci.*, Venkatasubramanian, K., Constantinides, A., and Vieth, W.R. (Eds.). New York Academy of Science, p. 310, 1983.
2. Quinn, M.J. and Sherlock, J.C. The correspondence between U.K. "action levels" for lead in blood and in water. *Food Addit. Contam.*, 7(3), 387–424, 1990.
3. Moore, M.R. Plumbosolvency of waters. *Nature*, 243, 222–223, 1973.

4. World Health Organization (WHO). Report of the 30th Meeting of the Joint FAO/WHO. Expert Committee on Food Additives. Geneva and Rome, World Health Organization, 1987.
5. Mushak, P. and Crocetti, A.F. Determination of numbers of lead-exposed American children as a function of lead source: Integrated summary of a report to the U.S. Congress on childhood lead poisoning. *Environ. Res.*, 50, 210–229, 1989.
6. Rabinowitz, M.B., Wetherill, G.W., and Kopple, J.D. Kinetic analysis of lead metabolism in healthy humans. *J. Clin. Invest.*, 58, 260–270, 1976.
7. Gilfillan, S.C. Lead poisoning and the fall of Rome. *J. Occup. Med.* 7, 53, 1965.
8. Syracuse Research Corporation Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile for lead. Public Health Service/U.S. Environmental Protection Agency, 1990.
9. Baker, E.L., Feldman, R.G., White, R.A., Harley, J.P., Niles, C.A., Dinse, G.E., and Berkey, C.S. Occupational lead neurotoxicity: A behavioral and electrophysiological evaluation. Study design and year one result. *Br. J. Ind. Med.*, 41, 352–361, 1984.
10. Lester, M.L., Horst, R.L., and Thatcher, R.W. Protective effects of zinc and calcium against heavy metal impairment of children's cognitive function. *Nutr. Behav.*, 3, 145–161, 1986.
11. International Agency for Research on Cancer (IARC). Chemicals, industrial processes and industries associated with cancer in humans. In IARC monographs (vols 1–29), *Eval. Carcinog. Risk. Chem. Hum.*, 149, 1982.
12. Cotton, F.A. and Wilkinson, G. Zinc, cadmium and mercury. In *Advanced Inorganic Chemistry*, Interscience Publishers, 503, 1972.
13. Riihimaki, V. Cadmium. In: *The Hazards to Health of Persistent Substances in Water. Long term program in environmental pollution control in Europe* (Annex to a report), World Health Organization, 1972.
14. Lymburner, D.B. The production, use and distribution of cadmium in Canada. In: *Environmental contaminants inventory study No. 2. Centre for Inland Waters* (Directorate), Report series no. 39, Ottawa, Canada, 1974.
15. Butterworth, J., Lester, P., and Nickless, G. Distribution of heavy metals in the Severn Estuary. *Mar. Poll. Bull.*, 3, 72, 1972.
16. Hiatt, V. and Huff, J.E. The environmental impact of cadmium: An overview. *Int. J. Environ. Stud.*, 7, 277–285, 1975.
17. Fleischer, M., Sarofim, A.F., Fassett, D.W., Hammond, P., Shacklette, H.T., Nisbet, I.C., and Epstein, S. Environmental impact of cadmium: A review by the panel on hazardous trace substances. *Environ. Health Perspect.*, 7, 253–323, 1974.
18. Friberg, L., Piscator, M., Nordberg, G.F., and Kjellstrom, T. *Cadmium in the environment*, 2nd Edition. CRC Press, Cleveland, OH, 1974.
19. Bernard, A. and Lauwerys, R. Cadmium in human populations. *Experientia*, 40, 143–152, 1984.
20. Schroeder, H.A. and Balassa, J.J. Abnormal trace metals in man—cadmium. *J. Chronic Dis.*, 14, 236–258, 1961.
21. Gleason, M. *Clinical toxicology of commercial products*, 3rd Edition. Williams and Williams, Baltimore, MD, 1969.
22. World Health Organization. *Environmental Health Criteria for Cadmium*, WHO, 1974.
23. Murata, I., Hirano, T., Saeki, Y., and Nakagawa, S. Cadmium enteropathy, renal osteomalacia (“Itai-Itai” disease) in Japan. *Bull. Soc. Int. Chir.*, 1, 34, 1970.
24. World Health Organization. Technical documents on arsenic, cadmium, lead, manganese and mercury. In: *The Hazards to Health of Persistent Substances in Water. Long term program in environmental pollution control in Europe* (Annex to a report), World Health Organization, Copenhagen, 1972.
25. Jonasson, I.R. and Boyle, R.W. *Geochemistry of Mercury. Mercury in Man's Environment*.: The Royal Society of Canada, p. 22, 1971.
26. U.S. Environmental Protection Agency (US-EPA). *Drinking Water Criteria Document for Mercury*. Environmental Criteria and Assessment Office, Final draft. Cincinnati, OH, p. 22, 1985.
27. Jensen, S. and Jernelev, A. Biological methylation of mercury in aquatic organisms. *Nature*, 223, 753–754, 1969.
28. Jernelev, A., Lander, R.L., and Larsson, T. Swedish perspectives on mercury pollution. *J. Water Pollut. Control Fed.*, 47, 810–822, 1975.
29. Suzuki, T. and Tanaka, A. Absorption of metallic mercury from the intestine after rupture of Miller-Abbot Balloon. *Ind. Med.*, 13, 52–58, 1971.
30. Skerfving, S. and Vostal, J. Symptoms and signs of intoxication. In: *Mercury in the Environment*, Friberg, L. and Vostal, J. (Eds.). CRC Press, Cleveland, OH, p. 93, 1972.
31. Bakir, F. Methylmercury poisoning in Iraq. *Science*, 181, 230–241, 1973.

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32. National Council on Radiation Protection and Measurements. Measurement of Radon and Radon Daughters in Air, NCRP report no. 97. Bethesda, MD, 1988.
33. King, P.T., Michel, J., and Moore, W.S. Ground water geochemistry of ^{228}Ra , ^{226}Ra and ^{222}Rn . *Geochim. Cosmochim. Acta*, 46, 1173–1182, 1982.
34. Nazaroff, W.W., Doyle, S.M., Nero, A.V., and Sexton, R.G. Potable water as a source of airborne ^{222}Rn in U.S. dwellings: A review and assessment. *Health Phys.*, 52, 281–295, 1987.
35. United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). Sources, Effects and Risks of Ionizing Radiation. Report to the General Assembly, New York, United Nations, 1988.
36. Gosink, T.A., Baskaran, M., and Holleman, D.F. Radon in the human body from drinking water. *Health Phys.*, 59(6), 919–924, 1990.
37. Hursh, J.B., Morken, D.A., Davis, R.P., and Lovass, A. The fate of radon ingested by man. *Health Phys.*, 11, 465–468, 1965.
38. Cross, F.T., Harley, N.H., and Hofmann, W. Health effects and risks from ^{222}Rn in drinking water. *Health Phys.*, 48(5), 649–670, 1985.
39. Abernathy, C., Calderon, R.L., and Chappel, W.R. *Arsenic Exposure and Health Effects*. Elsevier, London, UK, 1999.
40. Rashid, M.H. and Mridha, A.K. Arsenic contamination in groundwater in Bangladesh. In: *Sanitation and Water for All*, 24th WEDC Conference, Islamabad, Pakistan, pp. 162–165, 1998.
41. World Health Organization (WHO). Arsenic and Arsenic Compounds. In: *Environmental Health Criteria* 224, 13, pp. 5940–5948, 2005. Available at: <http://www.inchem.org/documents/ehc/ehc/ehc224.htm>.
42. Peryea, F.J. and Kammereck, R. Phosphate-enhanced movement of arsenic out of lead arsenate-contaminated topsoil and through uncontaminated subsoil. *Water, Air, Soil Pollut.*, 93(1–4), 243–254, 1997.
43. Abedin, M.J., Feldmann, J., and Meharg, A.A. Uptake kinetics of arsenic species in rice plants. *Plant Physiol.*, 128(3), 1120–1128, 2002.
44. Lee, R.B. Selectivity and kinetics of ion uptake by barley plants following nutrient deficiency. *Ann. Bot.*, 50, 429–449, 1982.
45. Smith, A.H., Lingas, E.O., and Rahman, M. Contamination of drinking-water by arsenic in Bangladesh: A public health emergency. *Bull. WHO.*, 78, 1093–1103, 2000.
46. Tondel, M., Rahman, M., Magnuson, A., Chowhury, I.A., Faruquee, M.H., and Ahmad, S.A. The relationship of arsenic levels in drinking water and the prevalence rate of skin lesions in Bangladesh. *Environ. Health Perspect.*, 107, 727–729, 1999.
47. Domenico, P.A. *Physical and Chemical Hydrogeology*. Wiley, Canada, 1990.
48. Anderson, M.P. and Woessener, W.W. *Applied Groundwater Modeling*. Academic Press, California, 1992.
49. Freeze, A.R. and Cherry, J.A. *Groundwater*. Prentice-Hall, New Jersey, 1979.
50. Ferguson, J.E. *The heavy Elements: Chemistry, Environmental Impact and Health Effects*. Pergamon Press, New York, 1990.
51. Soderbergh, S. Director of “Erin Brockovich” movie, 2000. Available at [http://en.wikipedia.org/wiki/Erin_Brockovich_\(film\)](http://en.wikipedia.org/wiki/Erin_Brockovich_(film)).
52. Williams, R. *Waste Production and Disposal in Mining, Milling and Metallurgical Industries*. Miller Freeman Publications, 1975.
53. Kalin, M. The role of applied biotechnology in decommissioning mining operations. In: *Proceedings of the 13th Annual General Meeting of BIOMINET*, Ottawa, ON, Canada, pp. 103–120, 1997.
54. Gazea, B., Adam, K., and Kontopoulos, A. A review of passive systems for the treatment of acid mine drainage. *Miner. Eng.*, 9(1), 23–42, 1996.
55. Filion, M.P., Sirois, L.L., and Ferguson, K. Acid mine drainage research in Canada. *CIM Bull.*, 83, 33–44, 1990.
56. Hammack, R.W., Edenborn, H.M., and Dvorak, D.H. Treatment of water from open-pit copper mine using biogenic sulfide and limestone: A feasibility study. *Water Res.*, 28, 2321–2329, 1994.
57. Naja, G., Mustin, C., Volesky, B., and Berthelin, J. Biosorption study in a mining wastewater reservoir. *Intern. J. Environ. Pollut.*, 2008 (in press).
58. Murray, D.R. Soil Profile Development in Vegetated Uranium Tailings. Natural Resources Canada, Energy Technology Center CANMET, Division report, MRP-MRL, pp. 81–126, 1981.
59. Hedin, R.S. Treatment of acid coal mine drainage with constructed wetlands. In: *Wetlands Ecology, Productivity and Values; Emphasis on Pennsylvania*, Pennsylvania Academy of Sciences, PA, 1989.
60. Singer, P.C. and Stumm, W. Acidic mine drainage: the rate determining step. *Science*, 167, 1121–1123, 1970.

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61. Alloway, B.J. *Heavy Metals in Soils*. Blackie Academic & Professional, Glasgow, UK, 1995.
62. Environment Canada, Environmental Protection Service. Overview of the Surface Finishing Industry: Status of the Industry and Measures for Pollution Control. EPS 2/SF/1, Ottawa, Canada, p. 43, 1987.
63. O'Flaherty, F., Roddy, W.T., and Lollar, R.M. *The Chemistry and Technology of Leather*, Vol. II. Reinhold, New York, p. 293, 1958.
64. U.S. Environmental Protection Agency (US-EPA). *Guidance Manual for Leather Tanning and Finishing Pretreatment Standards*. pp. 2–3, 1986.
65. Di Perno, N. Physico-Chemical and Resource Management Options for a Canadian Leather Retanner. Mechanical engineering thesis. Montreal, Canada: McGill University, 1991.
66. Environment Canada, Environmental Protection Service. National Inventory of Sources and Emissions of Copper and Nickel. Air pollution control directorate (91976), report EPS-3-AP, pp. 81–84, 1981.
67. Gabbard, A. Coal combustion: Nuclear resource or danger. *ORNL Review*, 26, 3–4, 1993.
68. Department of Energy, U.S. Mercury Emissions Control R&D. U.S. Dept. of Energy (2006-01-18), Washington, DC, 2006.
69. Streets, D.G., Hao, J., Wu, Y., Jiang, J., Chan, M., Tian, H., and Feng, X. Anthropogenic mercury emissions in China. *Atmos. Environ.*, 39(40), 7789–7806, 2005.
70. Environment Canada, Environmental Protection Service. *Significance and Treatment of Dissolved Solids in Wastewaters from Canadian Steam Electric Stations*. Ottawa, ON, Canada, 1985.

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