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Toxic Effect of Metal Ions in Water Resources

Dr. Suranjana Chattopadhyay

I. Metal Ions in Water Resources

Water is the most important resource. Without water life is not possible. From a chemical point of view, water, H_2O, is a pure compound, but in reality, you seldom drink, see, touch or use pure water. Water from various sources contains dissolved gases, minerals, organic and inorganic substances. This photograph of Guilin shows the beauty of natural water. The rain curved an interesting landscape out of the lime stones in the area. Natural waters are often important parts of wonders of the world.

The total water system surrounding the planet Earth is called the *hydrosphere*. It includes freshwater systems, oceans, atmosphere vapors, and biological waters. The Arctic, Atlantic, Indian, and Pacific oceans cover 71% of the Earth surface, and contain 97% of all water. Less than 1% is fresh water, and 2-3 % is ice caps and glaciers. The Antarctic Ice Sheet is almost the size of North America continent. These waters dominate our weather and climate, directly and indirectly affecting our daily lives. They cover $3.35x10^8$ km^2. The four oceans have a total volume of $1.35x10^9$ km^3. Groundwater is an important part of the water system. When vapor is cooled, clouds and rain develop. Some of the rain percolates through the soil and into the underlying rocks. The water in the rocks is *groundwater*, which moves slowly. Dust particles and ions present in the air are nucleation center of water drops. Thus, waters from rain and snow also contain such ions: Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+. These cations are balanced by anions, HCO_3^-, SO_4^-, NO_2^-, Cl^-, and NO_3^-. The pH of rain is between 5.5 and 5.6.

Rain and snow waters eventually become river or lake waters. When the rain or snow waters fall, they interact with vegetation, top soil, bed rock, river bed and lake bed, dissolving whatever is soluble. Bacteria, algae, and water insects also thrive. Solubilities of inorganic salts are governed by the kinetics and equilibria of dissolution. The most common ions in lake and river waters are the same as those present in rainwater, but at higher concentrations. The pH of these waters depends on the river bed and lake bed. Natural waters contain dissolved minerals. Waters containing Ca^{2+} and Mg^{2+} ions are usually called *hard water*.

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II. Hydration and Hydrolysis of Metal Cations

a) Hydration

When sodium chloride dissolves in water, the sodium and chloride ions and the polar water molecules are strongly attracted to one another by ion-dipole interactions. The solvent molecules (water in this case) surround the ions removing them from the crystal and forming the solution. As the dissolving process proceeds, the individual ions are removed from the solid surface becoming completely separate, hydrated species in the solution.

In order to dissolve the sodium chloride in the water, three processes have to occur:

1. The water molecules must be separated (H-bonds must be broken)
2. the forces of attraction between the ions in the NaCl lattice must be broken
3. solute-solvent(ion-dipole)interactions must be formed

The overall enthalpy change in forming a solution is the sum of energy changes for each of these processes. Whether the dissolution process will be exothermic or endothermic depends on the relative magnitudes of the energy changes for the three steps. In general, a substance will be insoluble if the energy expended to break apart the solvent and solute particles is significantly greater than the energy given off when solute-solvent interactions are established.

b) Hydrolysis

Metal ions in aqueous solution behave as Lewis acids. The positive charge on the metal ion draws electron density from the O-H bond in the water. This increases the bond's polarity making it easier to break. When the O-H bond breaks, an aqueous proton is released producing an acidic solution. Most chemical elements are metallic and form simple aqua ions with the formula $[M(H_2O)_n]^{z+}$ when the oxidation state is 1, 2 or 3. With the higher oxidation states the simple aqua ions dissociate losing hydrogen ions to yield complexes that contain both water molecules and hydroxide or oxide ions, such as the vanadium(IV) species $[VO(H_2O)_5]^{2+}$. In the highest oxidation state only oxyanions, such as the permanganate (VII) ion, MnO_4^- are known.[1]

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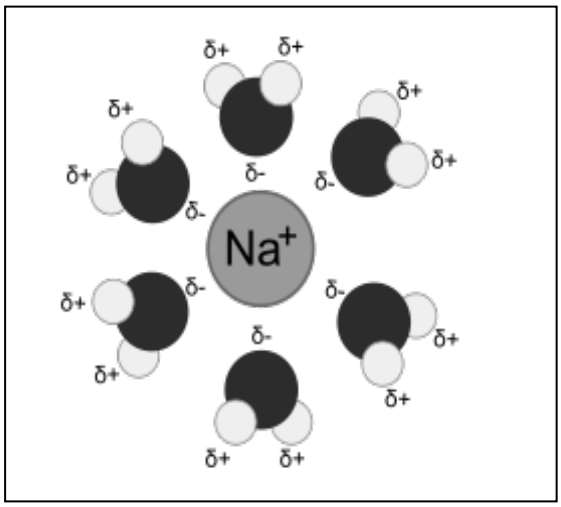

Fig. 1: Hydration of metal ion

c) Major Toxic ions and their effects

Environmental pollution by toxic metals occurs globally through military, industrial, and agricultural processes and waste disposal (Duffus, 2002). Fuel and power industries generate 2.4 million tons of As, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn annually The metal industry adds 0.39 million tons/yr of the same metals to the environment, while agriculture contributes 1.4 million tons/yr, manufacturing contributes 0.24 million tons/yr and waste disposal adds 0.72 million tons/yr. Metals, discharged or transported into the environment, may undergo transformations and can have a large environmental, public health, and economic impact.

The pollutants of concern include cadmium, lead, mercury, chromium, arsenic, zinc, cobalt and nickel as well as copper. They have a number of applications in basic engineering works, paper and pulp industries, leather tanning, petrochemicals, fertilizers, etc. Moreover, they have also negative impact on human health.

Cadmium is a metal of great toxicological concern. An important source of human exposure to cadmium is food and water, especially for the population living in the vicinity of industrial plants, from which cadmium is emitted to the air. In the case of exposure to occupational cadmium compounds, they are absorbed mainly by inhalation. However, an important source of cadmium in soils is phosphate fertilizers. Large amounts of cadmium are also introduced to soil together with municipal waste. The high mobility of cadmium in all types of soils is the reason for its rapid integration into the food chain. Daily intake of cadmium from food in most countries of the world is 10-20 mg. Through the gastrointestinal tract less than 10% cadmium is absorbed. An important source of human exposure to cadmium is food and water. In natural water, its typical concentration lies below 0.001 mg/dm^3, whereas, the upper limit recommended by EPA (Environmental Protection Agency) is less than 0.003 mg/dm^3. The maximum limit in drinking water is 0.003 mg/dm^3.

Cadmium accumulates in kidneys, pancreas, intestines and glands altering the metabolism of the elements necessary for the body, such as zinc, copper, iron, magnesium, calcium and selenium. Damage to the respiratory tract and kidneys are the main adverse effects in humans exposed to cadmium compounds. In humans exposed to fumes and dusts chronic toxicity of cadmium compounds is usually found after a few years. The main symptom of emphysema is that it often develops without preceding bronchitis. The second basic symptom of chronic metal poisoning is kidney damage. It includes the loss and impairment of smell, pathological changes in the skeletal system (osteoporosis with spontaneous fractures and bone fractures), pain in the extremities and the spine, difficulty in walking, the formation of hypochromic anemia. The most known 'Itai-Itai' disease caused by cadmium exposure is mixed osteomalacia and osteoporosis.

Lead is a toxic metal, which accumulates in the vital organs of men and animals and enters into the body through air, water and food. According to the WHO (World Health Organization) standards, its maximum limit in drinking water is 0.05 mg/dm^3 but the maximum discharge limit for lead in wastewater is 0.5 mg/dm^3. Lead is used as industrial raw material in the manufacture of storage batteries, pigments, leaded glass, fuels, photographic materials, matches and explosives. Lead being one of very important pollutants comes from wastewaters from refinery, wastewaters from production of basic compounds containing lead, wastewaters with the remains of after production solvents and paints.

The average collection of lead by an adult was estimated at 320-440 mg/day. Its cumulative poisoning effects are serious haematological damage, anaemia, kidney malfunctioning, brain damage etc. Chronic exposure to lead causes severe lesions in kidney, liver,

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lungs and spleen. Acute poisoning with inorganic lead compounds occurs rarely. In the case of acute poisoning in man, the symptoms are burning in the mouth, vomiting, abdominal cramps, diarrhea, constipation progressing to systolic, blood pressure and body temperature. At the same time there is hematuria, proteinuria, oliguria, central nervous system damage. Alkyl lead compounds are more toxic than inorganic lead connections. Tetraethyl lead toxicity manifested primarily in lead damage of the nervous system. Toxic effects of lead on the central nervous system are observed more in children. In adults, the effects of lead toxicity occur in the peripheral nervous system. Symptoms of chronic poisoning may vary. The acute form of poisoning known as lead colic is the general state of various spastic internal organs and neurological damage in the peripheral organs. Long-term lead poisoning can lead to organic changes in the central and peripheral nervous systems. Characteristic symptoms include pale gray skin colour and the lead line on the gums (blue-black border).

In nature, natural circulation of *mercury* vapour has a significant influence on the content of the soil and water. Elemental mercury in the rain water creates compounds by oxidation to divalent mercury. Both the chemical reaction, and under the influence of biological factors, and especially the activity of bacteria in the sediments of water bodies methyl and di-methyl mercury compounds are formed. Mercury, a fixed component of the waste water treatment that may be used for soil fertilization is a major threat to the inclusion of the metal in nutritional products. Drinking water may contain up to 300 ng Hg/dm^3, in highly industrialized areas it can reach up to 700 ng/dm^3. Daily consumption of mercury from food in the general population is less than 20 μg/day. 80% of mercury absorbed by the respiratory system is retained in the body. In the case of ingestion of inorganic mercury salts, salivation, burning in the throat, vomiting, bloody diarrhea, necrosis of the intestinal mucosa and kidney damage, leading to anuria and uremia can occur. The concentration of mercury vapour over 1 mg/m^3 damages lung tissue and causes severe pneumonia. The classic symptoms of metallic mercury vapour poisoning are manifested by tremor, mental disorders, inflammation of the gums. Its maximum limit in drinking water is 0.0005 mg/dm^3.

Chromium, occurring as Cr(III) or Cr(VI) in natural environments, is an important material resource, an essential micronutrient or toxic contaminant. Cr(III) is required for normal development of human and animal organisms but Cr(VI) activates teratogenic processes, disturbs DNA synthesis and can give rise to mutagenous changes leading to malignant tumours (WHO, Report 1998). Natural sources of chromium include weathered rocks, volcanic exhalations and biogeochemical processes and, in the man-polluted environment, mainly wastes after processing and utilization of chromium compounds. Chromium is an important and widely applied element in industry. The hexavalent and trivalent chromium is often present in electroplating wastewater. Other sources of chromium pollution are leather tanning, textile, metal processing, paint and pigments, dyeing and steel fabrication.

Chromium is associated with nucleic acids and is the subject to the concentration in liver cells. It plays an important role in the metabolism of glucose, certain proteins and fats, is part of enzymes and stimulates the activity of others. All compounds of chromium, with the exception of chromate, are rapidly cleared from the blood. Chromium also accumulates in the liver and kidneys. High concentrations of chromium, observed in the lungs of people exposed to this metal, indicate that at least part of chromium is stored in this organ in the form of insoluble compounds. The binding of chromium with the elements of the blood and transport of chromium by the blood depends mainly on its valence. Hexavalent chromium readily crosses the membranes of red blood cells and after reduction to trivalent chromium is bound to hemoglobin. The reduction of hexavalent to trivalent chromium, occurring within cells, considered as the activation of the carcinogenic chromium, increases because the probability of interaction of trivalent chromium on the DNA. Clinical signs of acute toxicity of chromium compounds are characterized by severe abdominal pain, vomiting and bloody diarrhea, severe kidney damage with hematuria leading to anuria, observed gastrointestinal ulceration. Chromium compounds and chromic acid are especially dangerous and cause serious damage to internal organs. Chronic exposure leads to chronic disorders in the body.

Arsenic is present in over 160 minerals. It is readily bio-accumulative and therefore its concentration in polluted waters may reach 430 mg/dm^3 in plants and 2.5 mg/dm^3 in fish.

Arsenic accumulates in tissues rich in keratin, like hair, nails and skin. Arsenic and its inorganic compounds can cause not only cancer of the respiratory system and skin, but also neoplastic lesions in other organs. Arsenic compounds enter the body from the gastrointestinal tract and through skin and respiratory system. Arsenic compounds have affinity for many enzymes and can block their action, and above all disturb the Krebs cycle. Inorganic arsenic compounds are more harmful than organic and among them AsH_3 and As_2O_3 should be mentioned. 70-300 mg of As_2O_3 is considered to be the average lethal dose for humans. The dose of 10-50 ppb for 1 kg of body weight can cause circulatory problems, resulting in necrosis and gangrene of limbs. The dominant effects of arsenic in humans are changes in the skin and mucous membranes as well as peripheral nerve damage. There are xerosis soles and palms, skin inflammation with ulceration. In addition, there is perforation of the nasal septum.

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In nature, *zinc* occurs in the form of minerals. An important source of zinc pollution is the burning of coal, petroleum and its products. Incineration of municipal solid waste can introduce about 75% zinc to urban air. Also, municipal wastewater generally contains significant amounts of zinc. The use of municipal and industrial waste in agriculture results in the accumulation of zinc in the surface layers of soil. Another source of this metal in soils are some preparations of plant protection products, as well as phosphatic fertilizers. The degree of toxicity of zinc is not big, but it depends on the ionic form, and changes under the influence of water hardness and pH. The daily average download of zinc by an adult is estimated at about 10-50 mg /day. The toxic dose is 150-600 mg. It is necessary for the proper functioning of living organisms and it is involved in the metabolism of proteins and carbohydrates. High doses of zinc cause damage to many biochemical processes followed by its deposition in the kidneys, liver, gonads. Kidneys play an important role in maintaining zinc homeostasis in the body. Zinc is relatively non-toxic to humans and animals. Hazard zinc mainly connected with secondary copper deficiency does not give specific symptoms.

Nickel is a moderately toxic element as compared to other transition metals. It is a natural element of the earth's crust; therefore its small amounts are found in food, water, soil, and air. Nickel occurs naturally in the environment at low levels. Nickel concentrations in the groundwater depend on the soil used, pH, and depth of sampling. In humans, the absorption of nickel from the gastrointestinal tract is less than 10%. Nickel taken with food and water is poorly absorbed and rapidly excreted from the body. It accumulates mainly in bones, heart, skin and various glands. Nickel inhalation of atmospheric air is largely accumulated in the lungs. Practically fatal or acute poisoning with nickel or its salts is not found. The most toxic compound is carbonyl nickel. An excess of inhaled nickel causes damage to the mucous membranes. Moreover, its symptoms are allergic disorders (protein metabolism disorder in plasma, changes in the chromosomes and changes in bone marrow and cancer. It is known that inhalation of nickel and its compounds can lead to serious problems, including, among others, respiratory system cancer. Moreover, nickel can cause skin disorder which is a common occupational disease in workers who handle its large amounts. Also dermatitis is the most common effect of chronic dermal exposure to nickel. Chronic inhalation exposure to nickel in humans also results in detrimental respiratory effects.

Copper is an essential nutritional element being a vital part of several enzymes. It is one of the components of human blood. The estimated adult dietary intakes are between 2 and 4 mg/day. The upper limit recommended by WHO for copper is less than 1.3 mg/dm^3. The maximum limit in drinking water is 0.05 mg/dm^3 (Fewtrell et al. 1996).The demand for copper is increased in pregnant women, children and the elderly. Good dietary sources of copper include animal liver, shellfish, dried fruit, nuts and chocolate. In some cases drinking water may also provide significant levels of copper. Copper in the body is involved in oxidation-reduction processes, acts as a stimulant on the amount and activity of hemoglobin, in the process of hardening of collagen, hair keratinization, melanin synthesis as well as affects on lipid metabolism and properties of the myelin sheath of nerve fibers. In animal cells it is mainly concentrated in the mitochondria, DNA, RNA, and the nucleus. Copper readily forms a connection with various proteins, especially those of sulphur. Although copper is an essential metal, it can, in some circumstances, lead to toxic effects including liver damage and gastrointestinal disturbances. Wilson's disease (also known as hepatolenticular degeneration), Indian Childhood Cirrhosis (ICC) are characterized by an accumulation of copper-containing granules within liver cells. Ingestion of high levels of copper salts is known to cause gastrointestinal upsets. Additionally, absorption of copper compounds by inhalation causes congestion of the nasal mucosa, gastritis, diarrhea and toxic symptoms such as chronic lung damage. Copper compounds act on the intact skin, causing it to itch and inflammation. They can cause conjunctivitis, ulceration and corneal opacity, nasal congestion and as well as sore throat and nasal septum.

III. Some Possible Remedies

Among different techniques used for removal of high concentrations of heavy metals, precipitation-filtration, ion exchange, reverse osmosis, oxidation-reduction, solvent extraction, as well as membrane separation should be mentioned (Hubicki,et al. 1999; Dąbrowski et al. 2004). However, some of the wastes contain substances such as organics, complexing agents and alkaline earth metals that may decrease the metal removal and result in unacceptable concentrations of heavy metals in the effluents.

Large toxicity of lead requires that its contents are reduced to the minimum (ppb level). To this end there are applied chelating ions with the functional phosphonic and aminophosphonic groups. Also weakly basic anion exchangers in the free base form can be used for selective removal of lead(II) chloride complexes from the solutions of pH in the range 4-6. Also a combined process of cation exchange and precipitation is often applied for lead(II) removal form wastewaters (Pramanik et al. 2009).

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