



GROUNDWATER POLLUTION AND TREATMENT WITH REFERENCE TO REMOVAL OF MINERAL IONS

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ABSTRACT

Groundwater will normally look clear and clean because the ground naturally filters out particulate matter. But, natural and human-induced chemicals can be found in groundwater. As groundwater flows through the ground, metals such as iron and manganese are dissolved and may later be found in high concentrations in the water. Industrial discharges, urban activities, agriculture, groundwater pumpage, and disposal of waste all can affect groundwater quality. Contaminants can be human-induced, as from leaking fuel tanks or toxic chemical spills. Pesticides and fertilizers applied to lawns and crops can accumulate and migrate to the water table. Leakage from septic tanks and/or waste-disposal sites also can introduce bacteria to the water, and pesticides and fertilizers that seep into farmed soil can eventually end up in water drawn from a well. Or, a well might have been placed in land that was once used for something like a garbage or chemical dump site. In any case, if you use your own well to supply drinking water to your home, it is wise to have your well water tested for contaminants.

Some of the major sources of groundwater pollution include storage vessels and reservoirs of petroleum products, storage vessels or chemicals, septic systems, hazardous waste sites, landfills, agricultural fields with high amounts of unabsorbed fertilizers, pesticides, and other chemicals.

Saline Ingress following over drafting of aquifers or natural leaching from naturally occurring deposits are natural sources of groundwater pollution. Leaching of minerals like arsenic and fluoride from their crystal lattice due to geological disturbance causes heavy groundwater contamination. While concern over groundwater contamination has focused on pollution associated with human activities, in many cases, groundwater contamination is related to private sewage disposal systems, land disposal of solid waste, municipal wastewater, wastewater impoundments, land spreading of sludge, brine disposal from the petroleum industry, mine wastes, deep-well disposal of liquid wastes, animal feedlot wastes, and radioactive wastes. Interactions between groundwater and surface water are complex. Consequently, groundwater pollution, sometimes referred to as groundwater contamination, is not as easily classified as surface water pollution. By its very nature, groundwater aquifer are susceptible to contamination from sources that may not directly affect surface water bodies. A spill or ongoing release of chemical or radionuclide contaminants into soil can contaminate the aquifer below, defined as a toxin plume.

INTRODUCTION

In order to address groundwater pollution control at the national level, the “**Water Pollution Prevention Law**” was amended in 1989 and set regulations on groundwater quality management. Four elements of groundwater quality management were determined in the law: (i) implementation of regular water quality monitoring by provincial government; (ii) prohibition of discharging hazardous wastewater into the ground by industry; (iii) mandatory notification for the establishment of facilities treating hazardous materials (notification by industry and examination by the governor), and (iv) implementation of emergent measures for accidental groundwater pollution (notification by industry and examination by

the governor). Of the four policy measures, three are for the prevention of pollution, while the other is for mitigation. In addition to those measures, in order to support these groundwater pollution policies, the **Environmental Standard for Groundwater Contamination** was established in 1997. In order to effectively conduct regular groundwater quality monitoring within the limited budget, there are three types of survey with different purposes: (i) a baseline survey of 240 wells in a 4-year period (survey of a quarter of wells per year); (ii) a survey of wells surrounding contamination points to detect the source and spread of contamination; and (iii) a periodical survey to monitor annual variation of the contaminants in detected cases.[1]

Waste generation is an inevitable consequence of industrial development. The storage of industrial and domestic waste in landfill sites can lead to significant groundwater pollution problems by leachate infiltration. Geomaterials can be a solution for waste management, using them as an engineered barrier. This work centered upon the development of new materials (GM1, GM2, and GM3) based on clay, activated carbon, cement, and polyvinyl alcohol polymer for the containment of stored waste and studied their performance through the trapping of inorganic pollutants. The high clay content (80%) was used for the GM1 preparation. (Pb^{2+} , Cd^{2+}) heavy metal retention properties were assessed by sorption isotherms onto geomaterials.[2] The lead sorption isotherm study showed that GM1 with the highest clay and lowest activated carbon contents and with a larger surface area is very efficient for the metal ion trapping. Indeed, lead adsorbed amount for GM1 Q_a is 77.40 mg/g and for GM2 and GM3 is about 43.54

and 37.71 mg/g. The total mass of dissolved constituents is referred to as the total dissolved solids (TDS) concentration. In water, all of the dissolved solids are either positively charged ions (cations) or negatively charged ions (anions). The total negative charge of the anions always equals the total positive charge of the cations. A higher TDS means that there are more cations and anions in the water. With more ions in the water, the water's electrical conductivity (EC) increases. By measuring the water's electrical conductivity, we can indirectly determine its TDS concentration. At a high TDS concentration, water becomes saline. Water with a TDS above 500 mg/l is not recommended for use as drinking water (EPA secondary drinking water guidelines). Water with a TDS above 1,500 to 2,600 mg/l (EC greater than 2.25 to 4 mmho/cm) is generally considered problematic for irrigation use on crops with low or medium salt tolerance.[3]

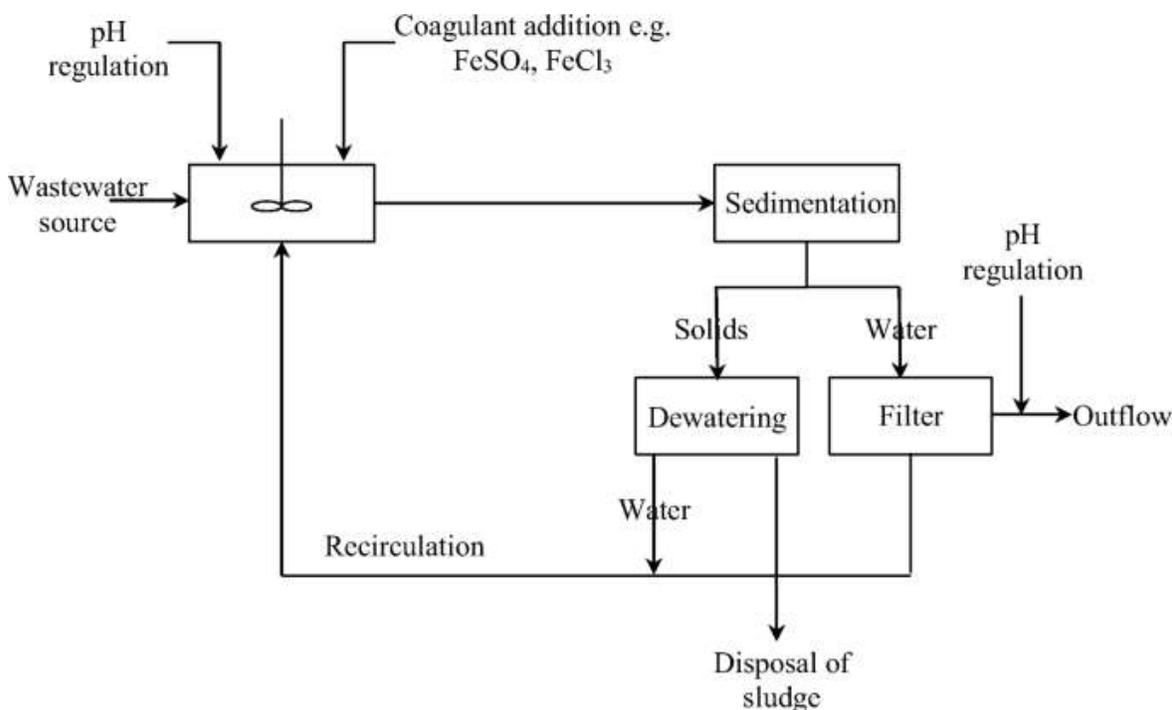


Fig.1: Removal of heavy metal ions

The removal of ferrous iron (Fe(II)) in groundwater has been generally achieved by simple aeration, or the addition of an oxidizing agent. Aeration has been shown to be very efficient in insolubilization ferrous iron at a pH level greater than 6.5. In this study, pH was maintained over 6.5 using limestone granules under constant aeration to oxidize ferrous iron in groundwater in a limestone packed column. A sedimentation unit coupled with a membrane filtration was also developed to precipitate and filtrate the oxidized ferric compound simultaneously. Several

bench-scale studies, including the effects of the limestone granule sizes, amounts and hydraulic retention time on iron removal in the limestone packed column were investigated. It was found that 550 g/L of the 7-8 mesh size limestone granules, and 20 min of hydraulic retention time in the limestone packed column, were necessary for the sufficient oxidation of 40 mg/L of iron(II) in groundwater.[4] Long-term operation was successfully achieved in contaminated waters by removing the iron deposits on the surface of the limestone granule by continuous aeration from the

bottom of the column. **Periodic reverse flow** helped to remove caking and fouling of membrane surface caused by the continuous filtration. Recycling of the

treated water from the membrane right after reverse flow operation made possible an admissible limit of iron concentration of the treated water for drinking.

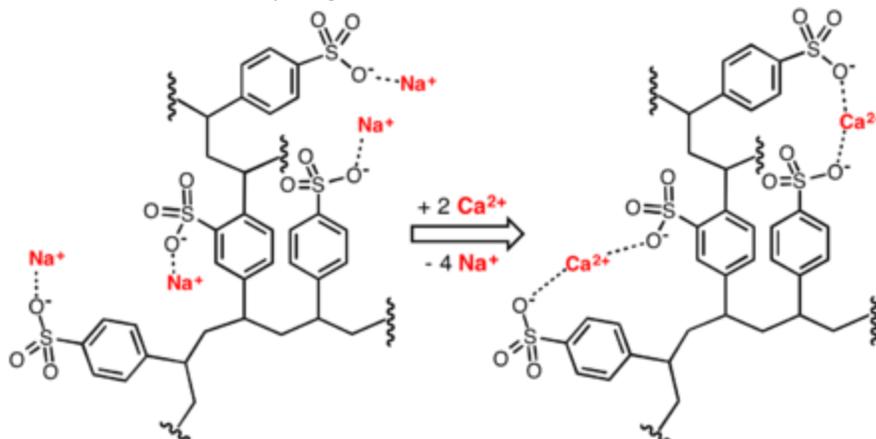


Fig.2: water softening

Groundwater can be contaminated with metals directly by infiltration of leachate from land disposal of solid wastes, liquid sewage or sewage sludge, leachate from mine tailings and other mining wastes, deep-well disposal of liquid wastes, seepage from industrial waste lagoons, or from other spills and leaks from industrial metal processing facilities (e.g., steel plants, plating shops, etc.). A variety of reactions may occur which influence the speciation and mobility of metal contaminants including acid/base,

precipitation/dissolution, oxidation/ reduction, sorption or ion exchange.[5] Precipitation, sorption, and ion exchange reactions can retard the movement of metals in groundwater. The rate and extent of these reactions will depend on factors such as pH, Eh, complexation with other dissolved constituents, sorption and ion exchange capacity of the geological materials, and organic matter content. Ground-water flow characteristics also influence the transport of metal contaminants.

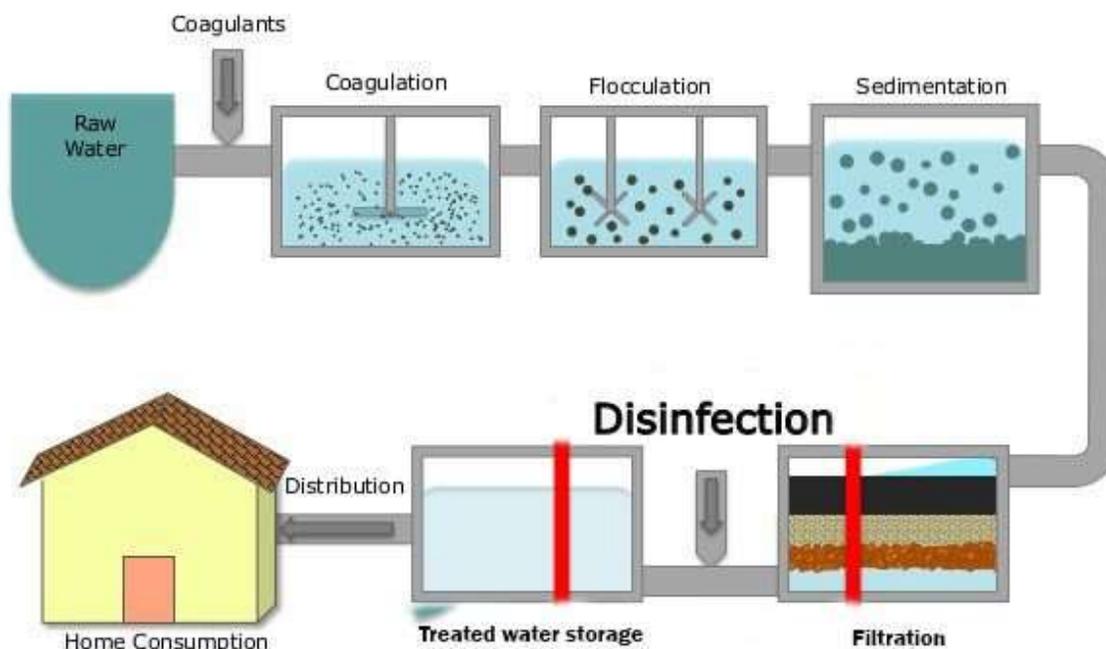


Fig.3: water purification steps

DISCUSSION

Ground-water samples are usually filtered with a 0.45 μ m filter prior to analysis for metals, though this is not always required and has recently been prohibited by many states and some U.S. EPA programs that require analysis of total metals. Interest in measurement of total metal concentrations (dissolved and particulate-associated metals) usually derives from concern about possible transport of metals adsorbed on mobile colloidal particles. Research indicates that significant colloid-facilitated transport of metals can occur only under a fairly specialized set of conditions, but the

conservative approach in monitoring system design is to try to capture any mobile colloids present. The problem with sampling groundwater without filtration is that particles from the well material, well slime coatings, or well pack may be sampled, and any subsequent analysis will not accurately reflect groundwater composition.[6] To avoid such artifacts, but still permit sampling that can capture any mobile colloids present in the groundwater, monitoring wells are purged before sampling to remove the casing water and obtain representative ground-water samples.

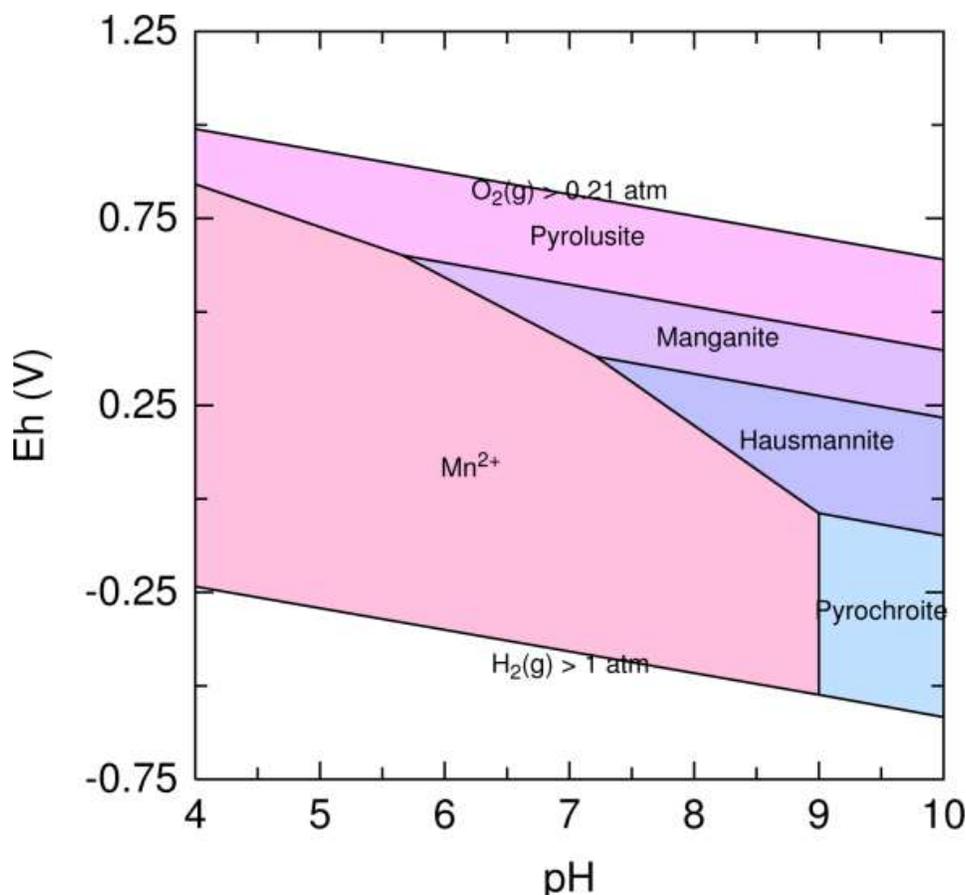


Fig.4: groundwater chemistry and treatment

Low-flow purging and sampling techniques have been developed to minimize sample disturbances that may affect analysis. The fate and transport of a metal in soil and groundwater depends significantly on the chemical form and speciation of the metal. The mobility of metals in ground-water systems is hindered by reactions that cause metals to adsorb or precipitate, or chemistry that tends to keep metals associated with the solid phase and prevent them from dissolving. These mechanisms can retard the movement of metals and also provide a long-term source of metal contaminants [7]. While the various metals undergo

similar reactions in a number of aspects, the extent and nature of these reactions varies under particular conditions. In Figure 2, for example, the extent of sorption of several metal cations and anions onto iron oxide is shown as a function of pH for a particular background electrolyte composition. It may be seen there that lead sorbs extensively at much lower pH values than zinc or cadmium.[8]

Lead

The primary industrial sources of lead (Pb) contamination include metal smelting and processing,

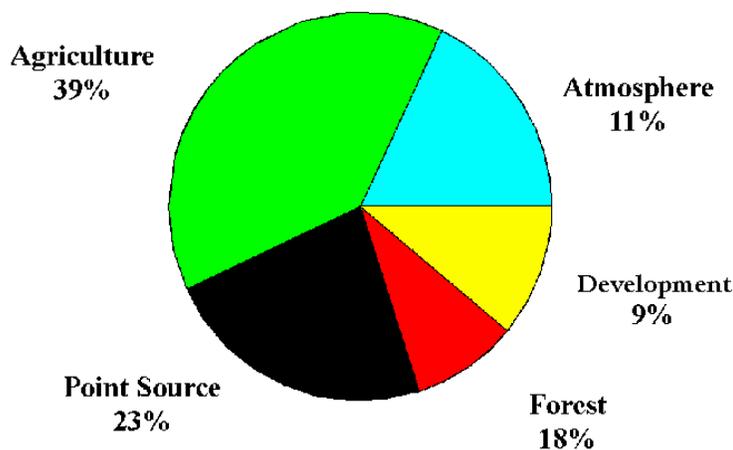


secondary metals production, lead battery manufacturing, pigment and chemical manufacturing, and lead-contaminated wastes. Widespread contamination due to the former use of lead in gasoline is also of concern. Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides, and leadmetal oxyanion complexes . Lead occurs most commonly with an oxidation state of 0 or +II. Pb(II) is the more common and reactive form of lead and forms mononuclear and polynuclear oxides and hydroxides.[9] Under most conditions Pb²⁺ and lead-hydroxy complexes are the most stable forms of lead .Low solubility compounds are formed by complexation with inorganic (Cl⁻, CO₃²⁻, SO₄²⁻, PO₄³⁻) and organic ligands (humic and fulvic acids, EDTA, amino acids) Lead carbonate solids form above pH 6 and PbS is the most stable solid when high sulfide concentrations are present under reducing conditions.

Most lead that is released to the environment is retained in the soil .The primary processes influencing the fate of lead in soil include adsorption, ion exchange, precipitation, and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater. The relatively volatile organolead compound tetramethyl lead may form in anaerobic sediments as a result of alkyllation by microorganisms .The amount of dissolved lead in surface water and groundwater depends on pH and the concentration of dissolved salts and the types of mineral surfaces present. In surface water and ground-water systems, a significant fraction of lead is undissolved and occurs as precipitates PbCO₃, Pb₂O, Pb(OH)₂, PbSO₄ sorbed ions or surface coatings on minerals, or as suspended organic matter. [10]

OVERALL BAY NUTRIENT SOURCES

NITROGEN



PHOSPHORUS

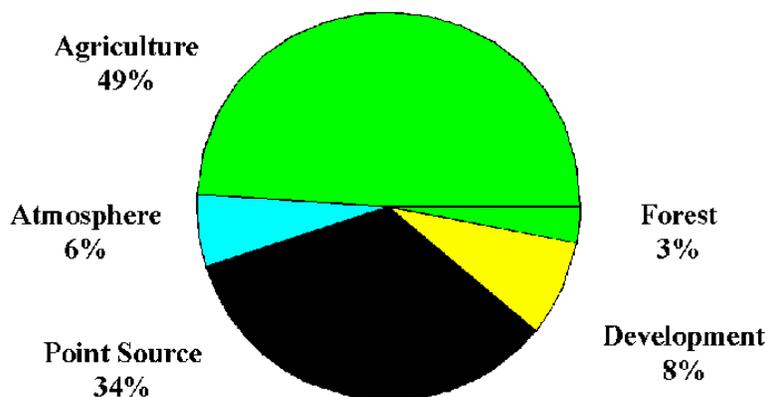


Fig.5: Phosphates in water

Chromium

Chromium(Cr) is one of the less common elements and does not occur naturally in elemental form, but only in compounds. Chromium is mined as a primary ore product in the form of the mineral chromite, $FeCr_2O_4$. Major sources of Cr contamination

include releases from electroplating processes and the disposal of chromium containing wastes. Cr(VI) is the form of chromium commonly found at contaminated sites.

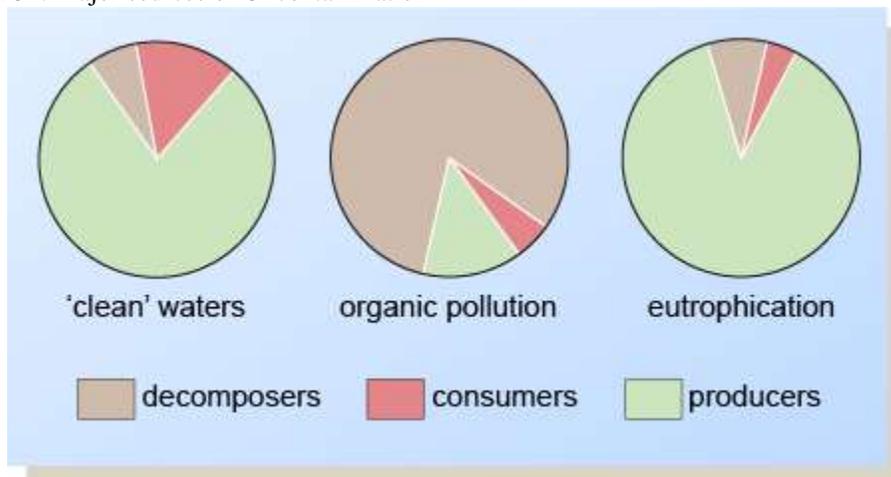
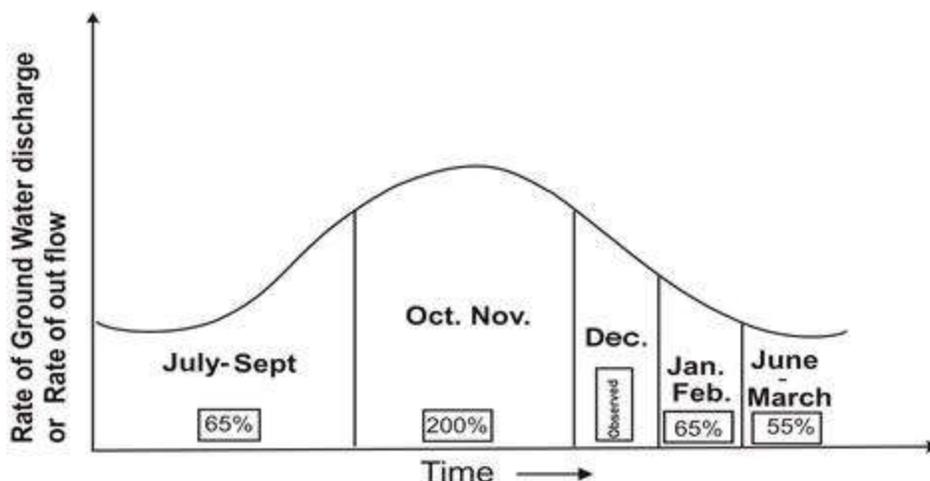


Fig.6: water pollution

Chromium can also occur in the +III oxidation state, depending on pH and redox conditions. Cr (VI) is the dominant form of chromium in shallow aquifers where aerobic conditions exist. Cr(VI) can be reduced to Cr(III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions often encountered in deeper groundwater. Major Cr(VI) species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) which precipitate readily in the presence of metal cations (especially Ba^{2+} , Pb^{2+} , and Ag^+). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Cr(III) is the dominant form of chromium at low pH (iron oxides are the most important removal mechanisms under most environmental conditions [11]). Arsenates can be leached easily if the amount of reactive metal in the soil is low. As(V) can also be mobilized under reducing conditions that encourage the formation of As(III), under alkaline and saline conditions, in the presence of other ions that compete for sorption sites, and in the presence of organic compounds that form complexes with arsenic.

Zinc

Zinc (Zn) does not occur naturally in elemental form. It is usually extracted from mineral ores to form zinc oxide (ZnO). The primary industrial use for Zinc is as a corrosion-resistant coating for iron or steel (Smith et al., 1995). Zinc usually occurs in the +II oxidation state and forms complexes with a number of anions, amino acids and organic acids. Zn may precipitate as $Zn(OH)_2(s)$, $ZnCO_3(s)$, $ZnS(s)$, or $Zn(CN)_2(s)$. Zinc is one of the most mobile heavy metals in surface waters and groundwater because it is present as soluble compounds at neutral and acidic pH values. At higher pH values, zinc can form carbonate and hydroxide complexes which control zinc solubility. Zinc readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations, and may coprecipitate with hydrous oxides of iron or manganese. Sorption to sediments or suspended solids, including hydrous iron and manganese oxides, clay minerals, and organic matter, is the primary fate of zinc in aquatic environments. Sorption of zinc increases as pH increases and salinity decreases.



General trend of rate of flow with time

Fig.7: mining of minerals in groundwater

Cadmium

Cadmium (Cd) occurs naturally in the form of CdS or CdCO₃. Cadmium is recovered as a by-product from the mining of sulfide ores of lead, zinc and copper. Sources of cadmium contamination include plating operations and the disposal of cadmium-containing wastes. The form of cadmium encountered depends on solution and soil chemistry as well as treatment of the waste prior to disposal. The most common forms of cadmium include Cd²⁺, cadmium-cyanide complexes, or Cd(OH)₂ solid sludge. Hydroxide (Cd(OH)₂) and carbonate (CdCO₃) solids dominate at high pH whereas Cd²⁺ and aqueous sulfate species are the dominant forms of cadmium at lower pH [12]

Cadmium is relatively mobile in surface water and ground-water systems and exists primarily as hydrated ions or as complexes with humic acids and other organic ligands. Under acidic conditions, cadmium may also form complexes with chloride and sulfate. Cadmium is removed from natural waters by precipitation and sorption to mineral surfaces, especially oxide minerals, at higher pH values (>pH 6). Removal by these mechanisms increases as pH increases. Sorption is also influenced by the cation exchange capacity (CEC) of clays, carbonate minerals, and organic matter present in soils and sediments. Under reducing conditions, precipitation as CdS controls the mobility of cadmium.

Copper

Copper (Cu) is mined as a primary ore product from copper sulfide and oxide ores. Mining activities are the major source of copper contamination in groundwater and surface waters. Other sources of copper include algicides, chromated copper arsenate (CCA) pressure treated lumber, and copper pipes.

Solution and soil chemistry strongly influence the speciation of copper in ground-water systems. In aerobic, sufficiently alkaline systems, CuCO₃ is the dominant soluble copper species. The cupric ion, Cu²⁺, and hydroxide complexes, CuOH⁺ and Cu(OH)₂, are also commonly present. Copper forms strong solution complexes with humic acids. The affinity of Cu for humates increases as pH increases and ionic strength decreases. In anaerobic environments, when sulfur is present CuS(s) will form. Copper mobility is decreased by sorption to mineral surfaces. Cu²⁺ sorbs strongly to mineral surfaces over a wide range of pH values. The cupric ion (Cu²⁺) is the most toxic species of copper. Copper toxicity has also been demonstrated for CuOH⁺ and Cu₂(OH)₂²⁺

Mercury

The primary source of mercury is the sulfide ore cinnabar. Mercury (Hg) is usually recovered as a by-product of ore processing. Release of mercury from coal combustion is a major source of mercury contamination. Releases from manometers at pressure measuring stations along gas/oil pipelines also contribute to mercury contamination. After release to the environment, mercury usually exists in mercuric (Hg²⁺), mercurous (Hg₂²⁺), elemental (Hg⁰), or alkylated form (methyl/ethyl mercury). The redox potential and pH of the system determine the stable forms of mercury that will be present. Mercurous and mercuric mercury are more stable under oxidizing conditions. When mildly reducing conditions exist, organic or inorganic mercury may be reduced to elemental mercury, which may then be converted to alkylated forms by biotic or abiotic processes. Mercury is most toxic in its alkylated forms which are soluble in water and volatile in air. Hg(II) forms strong complexes with a variety of both inorganic and organic

ligands, making it very soluble in oxidized aquatic systems. Sorption to soils, sediments, and humic materials is an important mechanism for removal of mercury from solution. Sorption is pH-dependent and increases as pH increases. Mercury may also be removed from solution by coprecipitation with sulfides

.Under anaerobic conditions, both organic and inorganic forms of mercury may be converted to alkylated forms by microbial activity, such as by sulfur-reducing bacteria. Elemental mercury may also be formed under anaerobic conditions by demethylation of methyl mercury, or by reduction of Hg(II). [13]

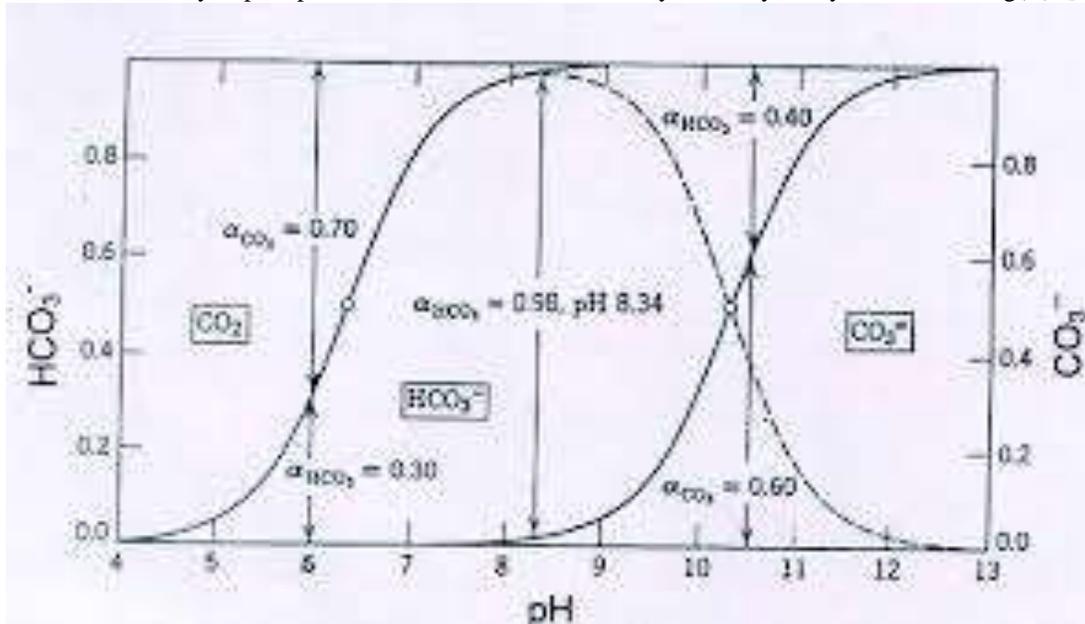


Fig.8:Water quality analysis

Metal cations are most mobile under acidic conditions while anions tend to sorb to oxide minerals in this pH range. At high pH, cations precipitate or adsorb to mineral surfaces and metal anions are mobilized. The presence of hydrous metal oxides of Fe, Al, Mn can strongly influence metal concentrations because these minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation. As noted in the previous section, sorption of metal cations onto hydrous oxides generally increases sharply with pH and is most significant at pH values above the neutral range, while sorption of metal anions is greatest at low pH and decreases as pH is increased. Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations on a mineral surface and is often used to indicate the affinity of soils for uptake of cations such as metals. Anion exchange capacity (AEC) indicates the affinity of soils for uptake of anions

RESULTS

Chemical Treatment

Chemical reactions can be initiated that are designed to decrease the toxicity or mobility of metal contaminants. The three types of reactions that can be used for this purpose are oxidation, reduction, and neutralization reactions. Chemical oxidation changes

the oxidation state of the metal atom through the loss of electrons. Commercial oxidizing agents are available for chemical treatment, including potassium permanganate, hydrogen peroxide, hypochlorite and chlorine gas. Reduction reactions change the oxidation state of metals by adding electrons. Commercially available reduction reagents include alkali metals (Na, K), sulfur dioxide, sulfite salts, and ferrous sulfate. Changing the oxidation state of metals by oxidation or reduction can detoxify, precipitate, or solubilize the metals. Chemical neutralization is used to adjust the pH balance of extremely acidic or basic soils and/or groundwater. This procedure can be used to precipitate insoluble metal salts from contaminated water, or in preparation for chemical oxidation or reduction. [14]

Chemical treatment can be performed ex situ or in situ. However in situ chemical agents must be carefully selected so that they do not further contaminate the treatment area. The primary problem associated with chemical treatment is the nonspecific nature of the chemical reagents. Oxidizing/reducing agents added to the matrix to treat one metal will also target other reactive metals and can make them more toxic or mobile. Also, the long-term stability of reaction products is of concern since changes in soil and water chemistry might reverse the selected reactions. Chemical treatment is often used as



pretreatment for S/S and other treatment technologies. Reduction of Cr(VI) to Cr(III) is the most common form of chemical treatment and is necessary for remediation of wastes containing Cr(VI) by precipitation or S/S. Chromium in its Cr(III) form is readily precipitated by hydroxide over a wide range of pH values. Acidification may also be used to aid in Cr(VI) reduction. Arsenic may be treatable by chemical oxidation since arsenate, As(V), is less toxic, soluble and mobile than arsenite, As(III). Bench-scale work has indicated that arsenic stabilization may be achieved by precipitation and coprecipitation with Fe(III) .[15]

CONCLUSION

Treatment by ion exchange

Ion exchange is a water treatment process commonly used for water softening or demineralization, but it also is used to remove other substances from the water in processes such as dealkalization, deionization, denitrification, and disinfection. With many other overlapping technologies available, it is important to determine whether ion exchange is the best choice in a given scenario. This attraction is used to remove dissolved ionic contaminants from water. The exchange process occurs between a solid (resin or a zeolite) and a liquid (water). In the process, the less desired compounds are swapped for those that are considered more desirable. These desirable ions are loaded onto the resin material. These resins can be used alone or in concert to remove ionic contaminants from water.

In the exchange of cations during water treatment, positively charged ions that come into contact with the ion exchange resin are exchanged with positively charged ions available on the resin surface, usually sodium.

In the anion exchange process, negatively charged ions are exchanged with negatively charged ions on the resin surface, usually chloride. Various contaminants — including nitrate, fluoride, sulfate, and arsenic — can all be removed by anion exchange.

Compared to other technologies, including continuous electrodeionization (CEDI), chromatography, ultrafiltration, and biological treatments, ion exchange is particularly suitable when trying to remove a specific low concentration pollutant, for example, removing boron from well water.[16]

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