



CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Water contamination

2.1.1 Introduction

Used water never really goes away. In fact, there never will be any more or any less water on Earth than there is right now, which means that all of the wastewater generated by our communities each day from homes, farms, businesses, and factories eventually returns to the environment to be used again. So, when wastewater receives inadequate treatment, the overall quality of the world's water supply suffers.

Wastewater has the potential to affect public health, the local economy, recreation, residential and business development, utility bills, taxes, and other aspects of everyday life. It is important to note its characteristics (that is, its components, strength, volume, and flow) and how certain characteristics can affect to lives.

2.1.2 Hydrological cycle

Water in the biosphere has three forms solid, liquid, and vapor. From Figure 1, it can be seen how the sun causes water evaporation from the surface water and causes evapotranspiration. The vapor rises into the atmosphere, while some is absorbed in soil by plants and then transferred into the atmosphere by the process, which is known as transpiration. The water vapor on the atmosphere condenses into tiny droplets, which cling to dust particles. These droplets for cloud and remain in the

atmosphere until they turn into precipitation and fall into the earth surface as rain, sleet, snow, or hail. The water, then, collects on lands and run off on the surface flows into receiving bodies of water. (ocean, streams, lakes, rivers, etc.). Some infiltrates (seeps) into the earth and joins with groundwater and collects in porous rock storing and supply water in aquifers. Some of the water is absorbed by plants and then transferred to the atmosphere again (NPS, 2005).

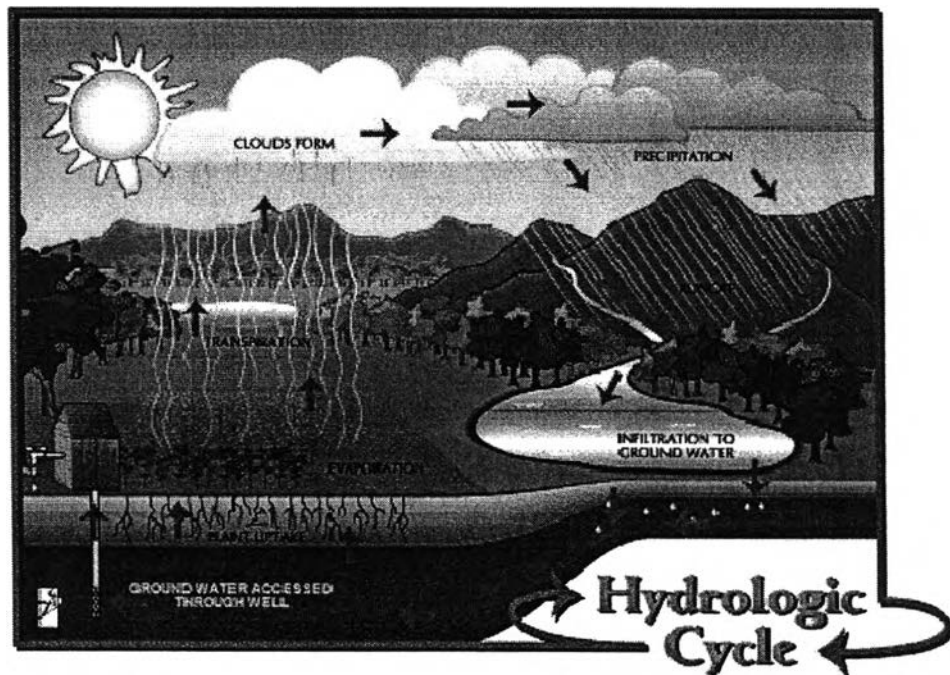


Figure 2.1 hydrologic cycle
Available from: NPS (2005)

As water moves through the hydrologic cycle, both natural processes and the actions of humans affect its quality. There are several ways for the substances to contaminate fresh water. For example, water is contaminated by runoff from storm water or snow melt, by seepage through the soil and by atmospheric transport during this cycle. Human activities are considered a major cause of water contamination, which is driven by the natural water cycle.

2.1.3 Sources of Contaminant

Inorganic minerals, metals, and compounds, such as sodium, potassium, calcium, magnesium, cadmium, copper, lead, nickel, and zinc are common in wastewater from both residential and nonresidential sources. They can originate from a variety of sources in the community including industrial and commercial sources, stormwater, and inflow and infiltration from cracked pipes and leaky manhole covers. Most inorganic substances are relatively stable, and cannot be broken down easily by organisms in wastewater.

Large amounts of many inorganic substances can contaminate soil and water. Some are toxic to animals and humans and may accumulate in the environment. For this reason, extra treatment steps are often required to remove inorganic materials from industrial wastewater sources. For example, heavy metals, which are discharged with many types of industrial wastewater, are difficult to remove by conventional treatment methods. Although acute poisonings from heavy metals in drinking water are rare, potential long-term health effects from ingesting small amounts of some inorganic substances over an extended period of time are possible.

2.2 Zinc

2.2.1 Introduction

Zinc is a naturally occurring element, which is found in the air, soil, and water and is present in all foods. In its pure element (or metallic) form, it is a bluish-white, shiny metal. Powdered zinc is explosive and may burst into flames if stored in damp places. Metallic zinc has many industrial uses. A common use is to coat iron or other metals to prevent rust and corrosion. It is also mixed with other metals to form alloys

such as brass and bronze. A zinc and copper alloy is used to make pennies in the United States. Metallic zinc is also used to make dry cell batteries.

Zinc can also combine with other elements, such as chlorine, oxygen, and sulfur, to form zinc compounds. Zinc compounds that may be found at hazardous waste sites include zinc chloride, zinc oxide, zinc sulfate, and zinc sulfide. Most zinc ore are found naturally in the environment is in the form of zinc sulfide. Zinc compounds are widely used in industry. Zinc sulfide and zinc oxide are used to make white paints, ceramics, and other product. Zinc oxide is also used in producing rubber. Zinc compounds, such as zinc acetate, zinc chloride, and zinc sulfate, are used in preserving wood and in manufacturing and dyeing fabrics. Zinc chloride is also the major ingredient in smoke from smoke bombs. Zinc compounds are used by the drug industry as ingredients in common products, such as vitamin supplements, sun blocks, diaper, rash oilments, deodorants, athlete's foot preparations, acne and poison ivy preparations, and antidandruff shampoos (ATSDR, 2003).

Consumption patterns

Zinc-base alloy: 38%; galvanizing: 38%; brass products: 15%; rolled zinc: 3%; zinc oxide: 3%; other, 3% construction materials, 45%; transportation, 25%; Machinery: 10%; electrical: 10%; other: 10% (1985) (Speclab, 2005).

2.2.2 Chemical and physical properties

Zinc usually occurs in the +2 oxidation state and forms complexes with a number of anion, amino acids and organic acids. It may precipitate as $Zn(OH)_2$, $ZnCO_3$, ZnS , or $Zn(CN)_2$. Zinc is one of the most mobile heavy metals in surface

waters and groundwater because it dissolves well at neutral and acidic pH values (Sparks, 1995).

Table 2.1 Chemical and physical properties of zinc

Descriptions	Values
Atomic number	30
Atomic mass	65.37 g.mol ⁻¹
Electronegativity according to Pauling	1.6
Density	7.11 g.cm ⁻³ at 20°C
Melting point	420 °C
Boiling point	907 °C
Vanderwaals radius	0.138 nm
Ionic radius	0.074 nm (+2)
Isotopes	10

At higher pH values, zinc can form carbonate and hydroxide complexes which are rarely dissolved. Zinc readily precipitates under reducing conditions and in highly polluted systems when it is present at very high concentrations, and may co-precipitate with hydrous oxides of iron or manganese (smith et al., 1995). Sorption to sediments or suspended solids, including hydrous iron and other oxides, clay minerals, and organic matter, is the primary fate of zinc in aquatic environments. Sorption of zinc increase as pH increases and salinity decreases.

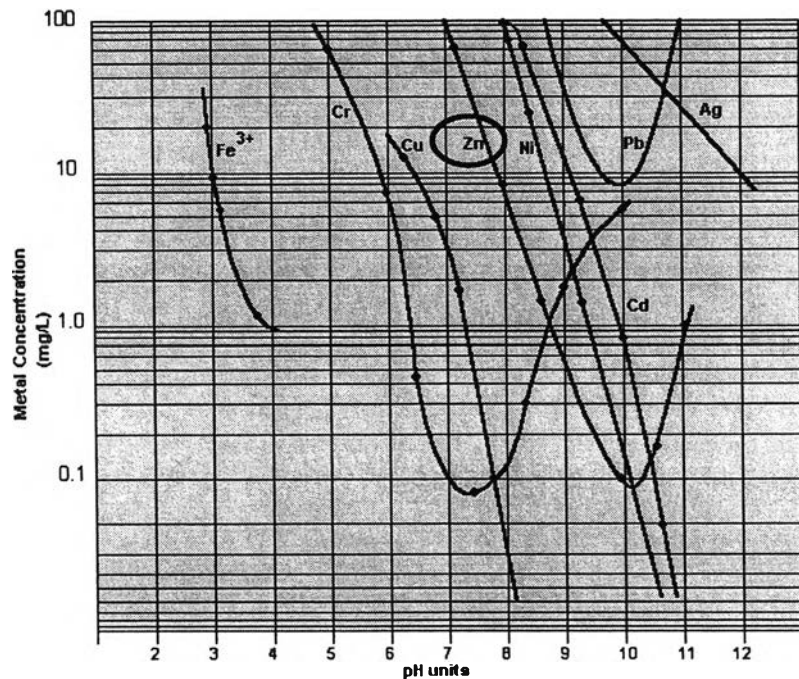


Figure 2.2 Heavy metal solubility
Available from: Hoffland Environmental Inc (2006)

2.2.3 Toxicology Information

2.2.3.1 Exposure Pathways

Zinc is an essential mineral needed by the body in small amounts. Humans are exposed to zinc compounds in food. The average daily zinc intake through the diet ranges from 5.2 to 16.2 milligrams (milligram = 0.001 gram). Zinc presents in most drinking water. Drinking water or other beverages may contain high levels of zinc if they are stored in metal containers or flow through pipes that have been coated with zinc to resist rust. If a person takes more than the recommended daily amount of supplements containing zinc, he may have higher levels of zinc exposure (ATSDR, 2003).

Zinc can enter the body through the digestive tract if ingested through food or drink water containing it. Zinc can also enter through the lungs if zinc dust or fumes

from zinc-smelting or zinc-welding operations are inhaled on the job. The amount of zinc that passes directly through the skin is relatively small. The most likely route of exposure near an NPL waste site is through drinking water containing a high amount of zinc. Zinc is stored throughout the body. Zinc increases in the blood and bones most rapidly after exposure. Zinc may stay in the bone for many days after exposure. Normally, zinc leaves the body in urine and feces (ATSDR, 2003).

Jobs where people are exposed to zinc include zinc mining, smelting, and welding; the manufacturing of brass, bronze, or other zinc-containing alloys; the manufacturing of galvanized metals; and the manufacturing of machine parts, rubber, paint, linoleum, oilcloths, batteries, some kinds of glass and ceramics, and dyes. People at construction jobs, automobile mechanics, and painters are also exposed to zinc (ATSDR, 2003).

2.2.3.2 Health effects of zinc (Lenntech, 2005)

Taking too much zinc into the body through food, water, or dietary supplements can also affect human health. The levels of zinc that produce adverse health effects are those much higher than the Recommended Daily Allowances (RDAs) for zinc of 15 mg/day for men and 12 mg/day for women. If large doses of zinc (10-15 times higher than the RDA) are taken by mouth even for a short time, stomach cramps, nausea, and vomiting may occur. Ingesting high levels of zinc for several months may cause anemia, damage the pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol. We do not know if high levels of zinc affect the ability of people to have babies or cause birth defects in humans.

Eating food containing very large amounts of zinc (1,000 times higher than the FDA) for several months caused many health effects in rats, mice, and ferrets, including anemia and injury to the pancreas and kidney. Rats that ate very large amounts of zinc became infertile. Rats that ate very large amounts of zinc after becoming pregnant had smaller babies. Putting low levels of certain zinc compounds, such as zinc acetate and zinc chloride, on the skin of rabbits, guinea pigs, and mice caused skin irritation. Skin irritation from exposure to these compounds would probably occur in humans. However, the Department of Health and Human Services (DHHS) and the International Agency for Research on Cancer (IARC) have not classified zinc for carcinogenicity. Based on incomplete information from human and animal studies, the EPA has determined that zinc is not classifiable as to its human carcinogenicity (ATSDR, 2003).

Consuming too little zinc is at least as important a health problem as consuming too much zinc. Without enough zinc in the diet, people may experience a loss of appetite, a decreased sense of taste and smell, decreased immune functions, slow wound healing, and skin sores. Too little zinc in the diet may also cause poorly developed sex organs and retarded growth in young men. If a pregnant woman does not get enough zinc, the babies may have growth retardation (ATSDR, 2003).

Zinc can be a danger to unborn and newborn children. When expecting mothers have absorbed large concentrations of zinc the children may be exposed to it through the blood or milk of their mothers.

Putting low levels of certain zinc compounds on the skin of rabbits, guinea pigs, and mice caused skin irritation. Skin irritation will probably occur in people. In the workplace environment zinc contagion can lead to a flu-like condition known

as metal fever. This condition will pass after two days and is caused by over sensitivity to zinc (Lenntech, 2005).

2.2.4 Regulations

The EPA recommends that drinking water should contain no more than 5 milligrams per liter of water (5 mg/L) because of taste. The EPA requires that any release of 1,000 pounds (or in some cases 5,000 pounds) be reported to the Agency.

To protect workers, the Occupational Safety and Health Administration (OSHA) has set an average limit of 1 mg/m³ for zinc chloride fumes and 5 mg/m³ for zinc oxide (dusts and fumes) in workplace air during an 8-hour workday, 40-hour workweek (ATSDR, 2003).

2.2.5 Zinc-Environmental Aspects (Fate & Transport)

Zinc enters the air, water, and soil as a result of both natural processes and human activities. Most zinc enters the environment as the result of human activities, such as mining, the purifying of zinc, lead, and cadmium ores, steel production, coal burning, and burning of wastes. These releases can increase zinc levels in the atmosphere. Waste streams from zinc, other metal manufacturing, zinc chemical industries, domestic wastewater, and run-off from soil containing zinc can discharge zinc into waterways. The level of zinc in soil increases mainly from the disposal of zinc waste from metal manufacturing industries and coal ash from electric utilities. In air, zinc is present mostly as fine dust particles. This dust eventually settles over land and water. Rain and snow aid in removing zinc from air. Most of the zinc in bodies of water, such as lakes or rivers, settles on the bottom. However, a small

amount may remain either dissolved in water or as fine suspended particles. The level of dissolved zinc in water may increase as the acidity of water increases. Some fish can accumulate zinc in their bodies if they live in water containing zinc. When zinc enters the bodies of these fish it is able to biomagnify up the food chain. Most of the zinc in soil is bound to the soil and does not dissolve in water. However, depending on the characteristics of the soil, some zinc may reach groundwater. Contamination of groundwater from hazardous waste sites has been noticed. Zinc may be taken up by animals eating soil or drinking water containing zinc. If other animals eat these animals, they will also accumulate in their bodies (ATSDR, 2003).

Zinc is not only a threat to animals, but also to plant species. Plants often have a zinc uptake that their systems cannot handle, due to the accumulation of zinc in soils.

On zinc-rich soils only a limited number of plants have a chance of survival. That is why there is not much plant diversity near zinc-disposing factories. Due to the effects upon plants zinc is a serious threat to the productions of farmlands. Despite this fact zinc-containing manures are still applied.

Finally, zinc can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The breakdown of organic matter may seriously slow down because of this.

2.3 Treatments options

Treatment options for groundwater and wastewater from Chapter 4 of the handbook: “Stabilization Technologies for RCRA Corrective Actions” describes data collection implementation, and technology indicate that the application for

groundwater pump-and-treat system (USEPA, 1991), a general review of methods to treat metals in groundwater, is presented in the Resource Recovery Project Technology Characterization Interim Report (MSE,1993). Specific information on precipitation is available in the report “Precipitation of Metals from groundwater” (NEESA, 1993). Bioremediation technologies are detailed in Bioremediation of Metals (Mattison, 1993). A summary of water treatment technologies is presented in Table 2.2

2.4 Foundry sand

2.4.1 Introduction

Within the definition of waste under the Environment Protection Act (1993), foundry sand is defined as a “by-product from casting operations”. Foundry sand primarily consists of clean, uniformly sized, high-quality silica sand or lake sand that is bonded to form molds for ferrous and nonferrous metal castings (USEPA, 2006). In foundries process of producing casting, molten metal is metal poured into molds. From these processes, (metal melting and pouring, and molding), sand casting is generated. Residuals consist of spent sand from molding and core-making, slag, and wastes from cleaning rooms, dust collectors or scrubbers. The major components in foundry sand are 70-80% quartz sand, 5-15% bentonite clay as the binder, 2-5% coal dust as a carbonaceous mold ingredient made of finely ground low-sulfur coal that improves the casting finish, and up to 4% moisture. However, the characteristic of the residuals vary from foundry to foundry due to the type of metal being poured, the type of casting process, and the technology employed, particularly the type of furnace and the type of finishing process (AFS, 1978).

Table 2.2 Summary of Treatment technologies for metal-bearing wastewater streams

Process	Applicable Waste streams	Stage of Development	Performance	Residuals Generated
Chemical Treatment Methods				
Precipitation	Aqueous streams; restrictions base on physical form, viscosity, and metal solubility	Well-developed, reliable process, suitable for automatic control.	Heavy metals: Cd, Cu, Pb, Hg, Ni, Ag, and Zn removed to 0.01 to 0.5 mg/l.	Effluent stream will require further processing to remove and dispose of precipitated solids.
Coagulation/ Flocculation	Aqueous streams; for ppb concentrations, two-stage process required; not readily applied to small, intermittent flows.	Well developed and readily available from commercial vendors.	Not considered a primary treatment but can achieve low residual levels.	Sludge requires secondary processing and disposal.
Reduction	Primarily aqueous chromebearing wastestreams,	Well developed.	Chromium removal to 0.01 mg/l. Sodium borohydride	Effluent stream will require further processing to remove

Process	Applicable Waste streams	Stage of Development	Performance	Residuals Generated
Floatation	<p>although sodium borohydride can treat most metals.</p> <p>Aqueous streams containing 100 mg/l or less of metals.</p> <p>Restrictions based on physical form, oil and grease content.</p>	Not fully developed for metals removal; primarily at pilot plant stage of development.	<p>able to remove Cu, Ni, Pb, Zn, Hg, Ag, Cd in the 0.01 to 1.0 mg/l range.</p> <p>Heavy metals Pb, Cu, Zn, Cr³⁺ removed to 0.03 to 0.4 mg/l</p>	<p>and dispose of reduced metal.</p> <p>Sodium borohydride introduces boron into the effluent stream.</p> <p>Requires posttreatment of metals-laden foam.</p>
Biological Treatment Methods				
Wetlands Treatment	Constructed wetlands remove metals by partitioning or	Pilot scale	May be used as final treatment for low concentrations of	Metals remain immobilized in wetland.

Process	Applicable Waste streams	Stage of Development	Performance	Residuals Generated
Bioreduction	precipitation. Bioreduction	Bench scale	heavy metals (10 mg/l or less). Tested for conversion of mercury salts to metal and Cr(VI) reduction.	Reduced metal requires post treatment for recovery or immobilization.
Thermal Treatment Methods				
Evaporation	Aqueous wastes with low nonvolatile metals content, or wastes with highly volatile metals content.	Well developed and widely available.	Can affect high-level recovery of volatile metals or significant volume reduction of aqueous wastes.	Brine.
Crystallization	Primarily used for wastes from electroplating and pickling that contains high levels of acids,	Well developed. Often used in conjunction with evaporation.	Can affect high-level recovery.	Sludges.

Process	Applicable Waste streams	Stage of Development	Performance	Residuals Generated
	water, or low-molecular-weight organics.			
Physical Treatment Technologies				
Membrane Separation	Aqueous waste streams containing 10 to 20% metals depending on the technology used.	Demonstrated technology for many process streams and waste streams.	Greater than 99% removal if properly used.	Concentrated brine requires treatment or disposal.
Liquid-Liquid Extraction	Aqueous, sludge, and solid wastes.	Limited use in hazardous waste field but widespread in mining and smelting industries.	Capable of yielding a solution that is 20 to 30 times more concentrated than feed.	Raffinated and regenerant stream may require posttreatment to remove residual extractant and metal.

Process	Applicable Waste streams	Stage of Development	Performance	Residuals Generated
Carbon Adsorption	Aqueous wastestreams containing metal ions at low pH. Effective in treating chelated metals as well as metal cations.	Largely experimental with some field applications for treating hexavalent chromium and mercury-containing wastestreams.	Used as a primary treatment for removal of hexavalent chromium. With a Cr^{6+} influent concentration of 6 ppm, effluent concentration of Cr^{6+} remained below 0.05 ppm.	Spent carbon requires disposal or reactivation.
Ion Exchange	Effective for treating dilute aqueous wastestreams as an end-of-pipe or polishing treatment.	Used in metal finishing and electroplating industries for recycling rinse solutions and concentrating waste metal solutions for efficient	Performance influenced by nature of functional group, ions available for exchange, and solution pH.	Regeneration solution requires treatment or disposal.



Process	Applicable Waste streams	Stage of Development	Performance	Residuals Generated
<p>Sorption on Inactive Biomass</p> <p>Electrolytic Treatment</p>	<p>Similar to ion exchange.</p> <p>Aqueous stream; high concentrations (greater than 1,000 ppm) are most efficiently removed.</p>	<p>treatment.</p> <p>Several products commercially available.</p> <p>Well developed and readily available from commercial vendors.</p>	<p>Similar to ion exchange but more efficient at low contaminant concentrations.</p> <p>Performance varies greatly depending on the application and the particular electrolytic unit used; some units may remove over 90% of metals such as Cu, Pb, Zn, Zu, Ag, and Cd.</p>	<p>Regeneration solution</p> <p>Generally the metal is recovered in a usable form and no residual solids are generated.</p>

2.4.2 Binder in foundry sand

Clay-bonded sands have provided the principal medium from which molds for castings have been produced for centuries. In essence the mold material consists of sand, usually silica in a quartz form, clay and water. The water develops the bonding characteristics of the clay, which binds the sand grains together. Under the application of pressure the mold material can be compacted around a pattern to produce a mold having sufficient rigidity to enable metal to be poured into it to produce a casting. When the mold is used in its moist condition it is referred to as green and the method of producing the molds as the green sand molding process. If the mold is dried at a temperature just above 100°C (212°F), the majority of the free moisture will be removed. This is the principal of the dry sand molding process. Removal of the free moisture is accompanied by a significant increase in the strength and rigidity of the mold. This enables the mold to withstand much greater pressures and so, traditionally, the dry sand process has been used in the manufacture of large, heavy castings. (Cast Metal Federation, 2005)

Clay-bonded sand

The principal addition to the sand is clay, which, in the presence of water, provides the bond necessary to develop mold strength. In addition to water and clay, the molding sand may contain organic materials to improve molding characteristics and mold properties (Cast metal federation, 2005). Low cost and available sorbent “clay” has adsorption capabilities for a variety of metals. Due to the size of the clay’s particle, which is smaller than 0.002 mm, it is classified as clay and has a very large specific surface area, giving it a tremendous capacity to absorb water and other substances. The large adsorptive surfaces results in the clay particles to coherence

together in a hard mass after drying. When wet, clay is sticky and can be easily molded.

According to their structure and composition, clays have been divided into a number of groups. There are four general types of clay used as binder in synthetic sands (AFS, 1978).

1. Fireclays, which is composed essentially of the mineral kaolinite ($\text{Al}_2\text{O}_3, 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$).

2. Bentonite, is a plastic clay derived usually by the decomposition of volcanic ash and consisting chiefly of the mineral montmorillonite. The color of bentonite clays varies from white to light green or light blue. When a dried bentonite is immersed in water, the former increases its volume or swells more than any other dried clay. When moist bentonites are dried, they shrink. When properly conditioned, clays are used in the construction of dams, reservoirs, ponds, or lagoons for preventing the seepage of water through them. The swelling property of the clays is utilized here to advantage to seal off the voids, thus reducing seepage flow by decreased permeability.

3. Fuller's earth is clay used primarily because of its bleaching qualities closely related to bentonite; it is used by some as bond clay.

4. Illite is a clay mineral found in many types of clay. However, illite is decomposition product of mica.

Clay's adsorption capabilities result from a net negative charge on the fine-grain silicate minerals' structure. The adsorption of positively charged species can neutralized this negative charge by giving clay the ability to attract and hold cations such as heavy metals.

2.4.3 Organic in foundry sand

In the iron foundry, there is not only clay-bonded sand but also one or more of a wide range of organic materials, added to make molds. The main purposes of additions are as follows (AFS, 1978):

1. To improve the surface finish
2. To prevent scabbing
3. To influence the bonding properties of the clay

The material that is widely used to improve the surface finish and prevent scabbing is coal dust. The improvement of the casting's surface finish occurs when coal dust is poured into an undried mold containing only sand and clay, it found that in certain areas, a layer of sand is firmly fixed to the casting which cannot be removed by vigorous brushing with a wire brush. The sand is cemented onto casting by a thin layer consisting of silicates, iron and aluminum.

During the casting process, the gas present in the pores of the mold is a mixture of air and steam which reacts with iron at high temperatures after the molten is poured into an undried mold which contains sand and moist clay only. The iron oxide is formed as the products of the reaction occur when the iron is liquid and contains 2% of silicon and 3% of carbon is uncertain at the condition of the temperature near the melting point of the metal. The oxide, which is chemically active, reacts easily with clay and sand to form mix silicates. After the casting cools, these silicates finally solidify, binding the sand grains to the casting.

Adding coal dust in the sand strongly reduces the decomposition products that fill the mold cavity and the formation of iron oxide is suppressed completely. The reasons adding coal dust to reduce the incidence of scabbing have put forward; the

main effect is that it increases hot plasticity. The coal dust used contains some 30% of volatile matter and most coals of this type partially melt at a temperature of 450 degree Celsius, producing a viscous liquid which persists over the range of temperature in which silica expands most rapidly.

However, foundry cores and molds are subjected to intense heat from the molten metal. The temperature of the mold-metal interface approaches 1000 degree Celsius. As a result, all organic materials undergo thermal degradation and oxidation. The nature and distribution of combustion and degradation products are complex and not entirely predictable. Because of the high temperature involved, all residual organic compounds are found in spent foundry sand in very small quantities. Therefore, despite the frequent use of originally toxic, irritant, and hazardous organic chemicals in molds or cores, spent sand after casting does not contain organic matter at hazardous levels.

The beneficial reuses of spent foundry sand are economically favorable, environmentally benign and technically equivalent to the material it is being replaced in the application.

2.4.4 Beneficial Reuse of Spent Foundry Sand

The iron and steel industries account for approximately 95 percent of the foundry sand being used for castings. Approximately 80 percent of the sand and dust generated each year by U.S. foundries is placed in landfills. The EPA estimates that the foundry industry has the potential to reuse or recycle 6 to 10 million tons of non-hazardous spent foundry sand each year. According to FIRST, a foundry recycling

nonprofit organization, the foundry industry could save \$100 to \$250 million in disposal costs by finding recycling outlets for this material.

Many states have developed beneficial reuse programs and regulations that allow spent foundry sand to be put to productive use. The beneficial reuse of foundry sand is increasing in a number of areas, including the transportation, construction, and environmental sectors. These industries can use large quantities of foundry sand as earth fills, hydraulic control barriers, and pavement system aggregates. Large foundries are typically the only generators capable of producing the amount of foundry sand necessary for these applications. Foundry sand from smaller generators can be used in other applications, such as the production of bricks, blocks, Portland cement, agricultural soil amendments, and other innovative products usually related to local markets. (USEPA, 2006)

2.5 Treatability testing

2.5.1 Introduction(Gavaskar et al., 1998)

The main purposes of treatability testing is

1. To estimate the half-life of the degradation reaction and determined the flow through the thickness of the reactive cell.
2. To evaluate the longevity of the wall.

Treatability test can be conducted in a batch or column (continuous) mode. Batch test are acceptable as an useful initial screening tool for evaluating different media or for assessing the degradability of the contaminants.

Another reason why, column tests are favored by researchers are as follows reasons:

1. Design parameters are determined under dynamic flow conditions. As concentrations of contaminants and inorganic change with the distance traveled through the reactive cell, they can be measured by installing a number of intermediate sampling ports along the half-lives measured through batch tests.
2. Nonlinear sorption to non-reactive sorption sites is better simulated in columns.
3. Reaction products may accumulate in the batch reactor, whereas they may be washed away in columns.

Various types of water may be used to run treatability tests:

1. Deionized water spiked with the targeted contaminant(s).
2. Contaminated wastewater from the site.

2.5.2 Batch Testing

Batch experiments generally are conducted by placing the media and contaminant-spiked water in conical tubes (PP with cap). These kinds of tests are useful screening tools because they can be run quickly and inexpensively. However, care should be taken in extrapolating the results to dynamic flow conditions. The results from batch experiment are considered when choosing the suitable medium for continuing the column experiment.

2.5.3 Column Testing

2.5.3.1 Column experiment (Gavaskar et al., 1998; Rensselaer Polytechnic Institute (RPI), 1996)

The main objective of a column test is to estimate the efficiency and reaction time of the medium, which is then used to design an appropriate flow through thickness for the reactive cell.

The necessary column residence time, volume of wastewater treated before breakthrough occurs and the shape of the column exhaustion curve are an important value for the column design.

Laboratory testing to establish the breakthrough curve is conducted for column adsorption design. At timed intervals, the effluent from a column is sampled. Time zero is when the solution is applied to the column.

At the beginning of the experiment, the adsorbent (in this study it is foundry sand) is fresh with all its adsorption sites. Essentially none of the material to be removed escapes from the column. As time passes, some of the adsorption sites are used up, and the concentration in the effluent rises.

From the result, the shape of the graph may vary considerably for different situations. Usually there is a long time before the effluent concentration rises sharply and then levels off. If all the sites were occupied, the inlet concentration and the outlet concentrations are expected to become the same.

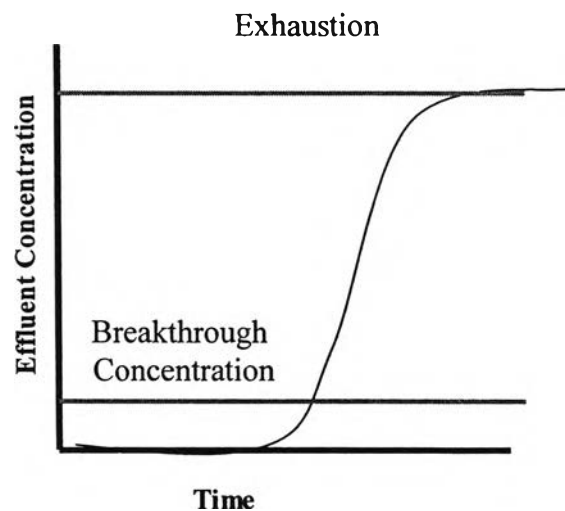


Figure 2.3 Breakthrough curve

The orange lines indicate the breakthrough concentration and exhaustion concentration. The breakthrough concentration is determined by the process specifications. This is the allowable concentration. If a pollutant is being removed, the breakthrough concentration might be the government regulation for wastewater dischargeable. (The concentration of the contaminant in the wastewater should meet the standard before being released.) For a commercial product where the column is removing color, the breakthrough concentration is determined by your specification for product quality. The point is that the breakthrough concentration is not some fundamental number but depends on the operator's decision.

The exhaustion concentration also depends on process considerations. If there are not enough workers on the night shift, the column may have to be removed in time for regeneration by the day shift so that it can be ready in time for the next day for use as a trail column. Note that the column could still adsorb more material. However, the operator will get little benefit by running for a longer time due to the

cost of labor, electricity, plant, etc. When the benefits are not worth the costs, the column is considered exhausted.

A practical way to design an adsorption column is to experiment with a laboratory column. The length of a full size column and of sufficient diameter to minimize wall effects can be scaled up from a laboratory experiment. This is merely a matter of increasing the area to match the volume to be treated. Even if the dimensions of the production column are undecided, operating the lab column until a breakthrough shows how much solution has been passed through sorbent. This leads to a simple calculation of the capacity of the sorbent. A major source of error is the effect of the flow rate because this determines contact time, and the approach to equilibrium takes times. (RPI, 1996)

2.5.3.2 Type of column systems

Down flow fixed beds may perform two functions: adsorption and filtration. However, excessive head losses necessitates frequent backwashing, and the economic gain of combining the two processes may be offset by decreased functional life of the bed and higher operating costs.

In up-flow fixed bed contactors, the influent enters through the bottom, and the treated effluent is drawn off at the top. The flow rate is kept low enough to allow the bed to remain stationary

2.6 Sorption

2.6.1 Background

Adsorption is the use of solids for substances removal from either gaseous or liquid solutions. This process involves the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. The adsorption phenomenon has become a useful tool for purification and separation. Its operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters.

Separation of a substance from solution accompanied by its accumulation or concentration at the surface of adsorbing phase (sorber) is the process of adsorption. The material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption is thus different from absorption, a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a "solution". The term sorption is a general expression encompassing both processes.

Van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface are mainly cause of Physical adsorption. Thus adsorbents are characterized first by surface properties such as surface area and polarity.

A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. The size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of

micropores is another important property for characterizing adsorptivity of adsorbents. (Slejko, 1985; Suzuki, 1990; and IAS, 2006)

2.6.2 Ion exchange

2.6.2.1 Principle

Ion exchange is the process where an insoluble substance removes ions of positive or negative charge from an electrolytic solution and releases other ions of like charge into the solution in a chemically equivalent amount.

Most of the cation exchange capacity of clay mineral is due to the permanent fixed charge at the clay surface, there is also a pH-dependent charge that can contribute to the exchange capacity. At low pH values (less than about 6), hydrogen ions are strongly bonded to oxygen atoms at crystal edges, and these sites are not available for cation exchange. However, as the pH increases and the aqueous hydrogen ion activity decreases, the bond with oxygen breaks releasing hydrogen into the solution, thereby creating new cation exchange sites.

At low pH values, H^+ is the major adsorbing, exchangeable cation, but as the pH increases and the H^+ activity decreases, the sites become more available for exchange with the major cations in solution.

The cation exchange capacity available to soil, water or groundwater will be a function of the amount of inorganic clay minerals and organic humus present in the solid phase. Material coarser than clay size ($2\mu m$) has a proportionally smaller surface area and does not add significantly to the cation exchange capacity.

Anion exchange may also occur on clay minerals, but to a much lesser extent than cation exchange because of the dominant fixed negative charge on the clay mineral surface. (Thunsiri, 2004)

2.6.2.2 Point of Zero Charge

Generally, at low pH value cationic hydroxyl species dominate whereas at high pH value soluble anionic hydroxyl species dominate. The minimum point of solubility corresponds to the point of zero charge (PZC) where the neutrally charged heavy metal hydroxide dominates, the equilibrium position of anionic neutral and cationic hydroxyl complexes (Entech Industries Pty Ltd,2005).

In conclusions, from the experiment the easy way to find out if there is ion exchange occurred in the column. Zinc ion from inlet solution will exchange with some ion from foundry sand which is causes zinc attach with foundry sand in the other hand the ion from foundry sand will release into the solution instead. Therefore, beside zinc from influent being sorbed by foundry sand in the column, there should have other substances that interact with zinc and exchange out from Foundry sand mix with the solution in the samples. Moreover, the tendency of its quantity should relate with the amount of zinc disappear from the water. However, the mechanisms occurred in the column can have more than one. For example, there might have ion exchange accompany with adsorption which result to the increasing of the capacity of the media.

2.7 Literature reviews

There are many studies using adsorbents for heavy metal removal, include commercial activated carbon (Netzer and Hughes, 1984; Reed and Arunacalam, 1994), activated carbon from low cost materials (Budinova et al., 1994; Periasamy and Namasivayam, 1994), EDTA coated activated carbon (Lu et al., 1993), Peat (D'Avila et al., 1991), fly ash (Diamadopouls, 1993) and lignite (Sllen and Brown, 1995).

Blowes et al. (1997) evaluated several kinds of sorbent (Fe-bearing solids, siderite, pyrite, coarse-grained elemental iron, and fine grained Fe). The results showed that Fe filing (fine grain) had the best efficiency to sorb Cr^{6+} because of its highest specific surface area. Low flow rates had better efficiency than the rapid ones.

Mellah et al. (1997) studied the operating parameters (agitation speed, temperature, particle and initial zinc concentration) that influence the rate of adsorption. The maximum monomolecular capacity Q_0 according to the Langmuir model was 52.91 mg/g for an initial zinc concentration of 300 mg/l at 20 °C.

Lee and Benson (2002) used foundry sands as reactive media in permeable reactive barriers to adsorb zinc at influent pH 4.0, the partition coefficients from the column tests were 4 or 5 times higher than those obtained from the batch sorption test because the solution pHs for the column test were higher than batch's. However, Benson's work didn't vary the flow rates or bed height to see the effectiveness of the sorption efficiencies.

Abollino et al. (2003) studied the sorption of 7 metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) on Na-montmorillonite was studied as a function of pH and in the presence of ligands to form complexes with the metals of interest. The pH variations

influenced to a greater extent the concentrations of Cu, Pb and Cr in the effluent. The results suggested that complexes formation hinders the sorption of the metals on the clay, in the following increasing order: $Mn \geq Pb \geq Cd \geq Zn \geq Ni \geq Cu \geq Cr$. The evaluation of the total capacity of Na-montmorillonite showed that this clay was a good sorbent of all the metals examined.

Katsumata et al. (2003) studied the column experiment for its ability to remove heavy metal from plating factory wastewater by montmorillonite, kaolin, tobermorite, mageneticite, silicagel and alumina as sorbents to wastewater containing Cd(II), Cr(VI) and Pb(II). They noticed that the removal efficiency tends to increase with increasing pH and decrease with increasing metal concentrations.

Thunsiri (2004) studied “utilization of foundry sand waste as heavy metal sorbent” in batch experiment by using four kinds of foundry sand, Siam Magotax Co., Ltd., Siam Nava Industry Co., Ltd., Siam Navaloha Foundry Co., Ltd., and Asian Autopart Co., Ltd.

Vijayaraghavan et al. (2004) packed bed up-flow column experiment was performed with an internal diameter of 2 cm. The bed height and flow rates were varied in order to investigate the ability of crab shell to remove nickel (II) ions from aqueous solution. The elution efficiency was greater than 99.1% in all seven cycles. The loss of sorption performance was observed as the cycles progressed, which was equally indicated by a decrease in breakthrough time, a broadening of the mass transfer zone, and a loss in sorbent weight. The increase in flow rate resulted in decreased nickel uptake, probably due to insufficient residence time of the solute in the column. The result showed that crab shell acts as an attractive treatment option for nickel bearing solutions.

Kundu and Gupta (2005) used iron oxide-coated cement as a medium to remove As(V) from water. Characteristic parameters such as the depth of the exchange zone, time required for exchange, adsorption rate, and adsorption capacity were calculated by the Bohart and Adams sorption model. The maximum adsorption capacity was 505.3 mg/L. The BDST model used in the evaluation of the column parameters gave results that were in good agreement with the experimental results. Breakthrough profiles were also in good agreement with the theoretical breakthrough profiles obtained that was incorporated into the Freundlich isotherm model. The greater the bed depth length the column had, the longer service time was occurred for the treatment. Likewise to the increasing of flow rate and initial concentration, these resulted to the decreasing of service time.

Vijayaraghavan et al. (2005) investigated eggshells for their ability to remove copper from aqueous solution in an up-flow packed column. The sorption performance of eggshell in the column was examined by varying the bed height (15-30.5 cm) and flow rate (5-20 ml/min.). A decrease in breakthrough time was observed as the cycles progressed. Both bed height and flow rate affected the copper sorption characteristics of the eggshell. The breakthrough time increased with an increase in the bed height. The effects of flow rate were also observed - at higher flow rates, the breakthrough curves became steeper, and as the flow rate increased, the mass transfer zone became shorter. At a low flow rate of 5 ml/min, a relatively higher copper uptake was observed and the uptake decreased as the flow rate increased. This behavior may be due to the insufficient time for the solute inside the column and diffusion limitations of the solute into the pores of the sorbent (Ko et al., 2000).

Thunsiri (2004) indicated that:

1. The studied indicated that the zinc concentration decreased as time passed for all pH of the solution.
2. The equilibrium concentrations were found within 24 hr.
3. The solution pH continued to increase as time progressed and stabilized within 24 hr. (equilibrium)
4. The result showed that waste foundry sand is effective for the removal of zinc via sorption and precipitation processes. Particularly, amount of zinc removed increased as solution pH increased.
5. The zinc removal efficiency by foundry sand using initial zinc concentration 50 mg/l are 5.12, 79.8, and 92.39% at initial pH 3.72, 6.59, and 8.01, respectively.
6. Clay, TOC, and total iron contain in waste foundry sand are responsible for the sorption of zinc. This provided more sorption site for zinc and caused the formation of zinc hydroxide.
7. This kind of foundry sand, Siam Nawa industry, when compared with the others three kinds of foundry sand, showed that has the best efficiency to remove zinc.



From others research described that the column experiment was designed follow from the studies above, four kinds of foundry sand, bed height (15-30.5 cm), flow rate (5-20 ml/min.), and up-flow packed column. And the results from these experiments indicate that the increase in flow rate resulted in decreased metals uptake, probably due to insufficient residence time of the solute in the column. The breakthrough time increased with an increase in the bed height. And the removal efficiency tends to increase with increasing pH and decrease with increasing metal concentrations.