

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Groundwater Contamination

Groundwater is an important source of water supply in Thailand. It is estimated that 95 percent of domestic water is obtained from groundwater sources (Ramnarong, 1991).

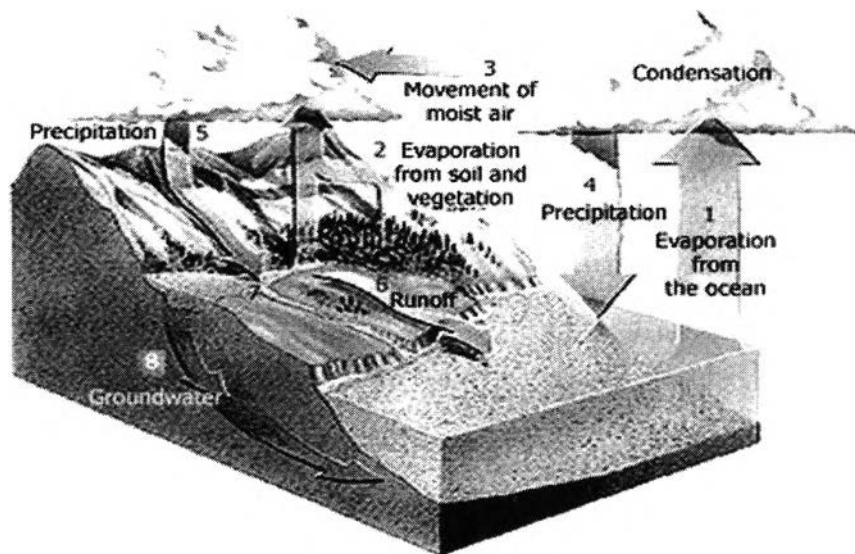


Figure 2.1 Fate of contaminant migration

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 such as steel plants, metal plating process and mining

operation. A variety of reactions occur which influence the speciation and mobility of metal contaminants including acid/base, precipitation/dissolution, oxidation/reduction, sorption or ion exchange. Precipitation, sorption, and ion exchange reactions can retard the movement of metals in groundwater. The rate and extent of these reactions depend on factors such as pH, complexation with other dissolved constituents, sorption and ion exchange capacity of the geological materials, and organic matter content.

Groundwater characteristics also influence the transport of metal contaminants. Domestic sewage, industrial effluents, and agricultural run-off all contribute to increasing pollution of surface, coastal, and ground water. Contamination may occur wherever the potential exists for transport to matter into the groundwater environment, either from the ground surface or by the drawing in natural contaminants from adjacent subsurface or surface water through the action of man. The typical range of Thailand's groundwater characteristic is shown in Table 1.

Table 2.1 Typical range of Thailand's groundwater characteristic (DPR 2003)

	Parameters	Units	Typical Range
PHYSICAL	Turbidity	JTU	20 - 150
	pH	-	3.7 - 9.2
CHEMICAL	Chloride	mg/l	4 - 7500
	Fe	mg/l	0.1 - 45
	Fluoride	mg/l	0.3 - 1.0
	Mn	mg/l	0 - 7.4
	Nitrate	mg/l	0.4 - 8.90
	Sulphate	mg/l	5.0 - 450
	Total solids	mg/l	0 - 5,500
	Zn	mg/l	0.5 - 75

Heavy metals are a group of contaminants that are highly toxic to humans, animals, and aquatic lives. Heavy metals are commonly found in many municipal and industrial wastes. The migration of contaminants from a waste disposal site usually involves one or more of the following processes:

- a) Advective, dispersive, and diffusive mass transport through the barrier,
- b) Chemical reactions within the soil solution,
- c) Interactions between the soil solution and the soil solids, such as adsorption, ion exchange, and precipitation and,
- d) Biodegradation

A range of technologies is available for the remediation of metal-contaminated soil and groundwater. Groundwater treatment techniques involved flushing and aboveground treatment, whereas treatment of contaminated soil has involved excavation and followed by ex situ treatment (solidification/ stabilization) or disposal. Low-cost, and effective, in situ methods are desired, and are being explored and tested with increasing interest.

Examples of in situ innovative technologies for metals remediation are redox manipulation, permeable treatment walls, biological treatment, phytoremediation, and electrokinetic techniques. Permeable treatment walls have shown promise in effectively reducing the toxicity and mobility of several heavy metals (Shoemaker et al. 1995, Benner et al. 1997).

## **2.2 Permeable Reactive Barrier**

A permeable reactive barrier is a new technology that remediates contaminated groundwater and soil without mass excavation, disposal or conventional

methods. Normally, permeable treatment walls are placed in the path of naturally flowing groundwater with metals, and the media in the permeable wall adsorbs the metals and immobilizes them within. Barriers can also be created by in situ redox manipulation technique.

Typical treatment media include granular iron, activated carbon, engineered bacteria, compost or peat, chemicals, and organophilic clays. Often, slurry walls are used to funnel the groundwater toward a reactive media gate. Special construction considerations are needed for installing treatment media to ensure the design life of the media and to be cost-effective. Since the media must be buried deep underground and below the groundwater table, geotechnical methods are quite useful in minimizing excavation volumes, eliminating dewatering, and reducing costs.

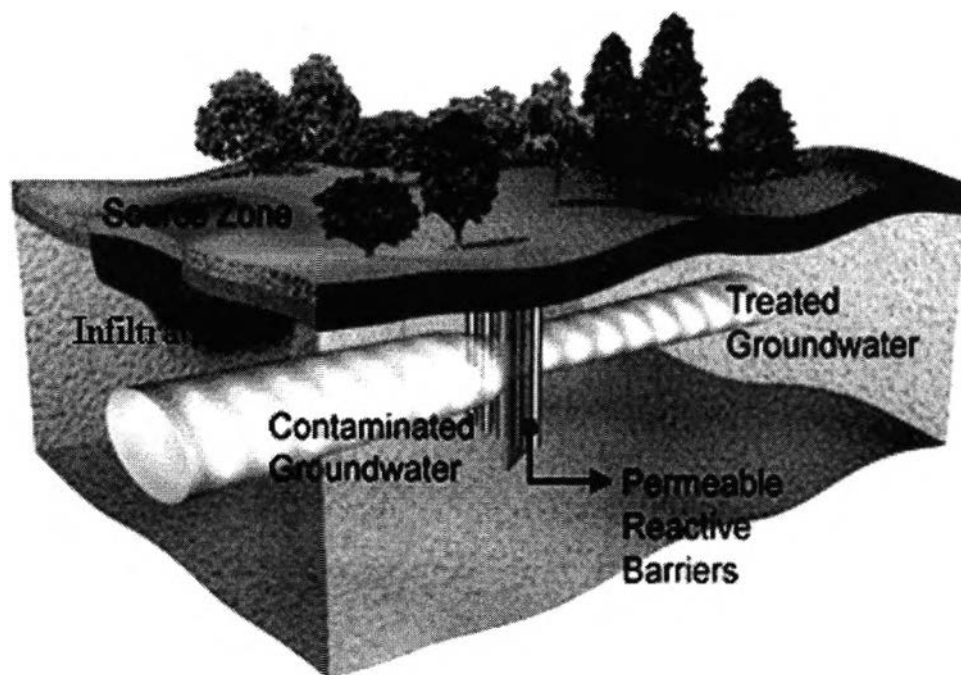


Figure 2.2 Schematic of permeable reactive barrier

In most cases, the least expensive method for installing funnel and gate is a slurry trench method. A slurry wall (e.g. soil-bentonite, cement-bentonite or soil-cement-bentonite) can provide the funnel to direct groundwater toward the reactive materials. A bio-polymer slurry trench can provide the permeable gate for the installation of the reactive media. The savings from this combination of methods are considerable including savings in excavation volumes, disposals costs, mobilization, and construction time. Slurry trenching methods have been proven to permit the installation of reactive iron, engineered bacteria, compost, carbon and other materials without significantly affecting the reactive potential of the media. In some cases, i.e. bio-treatment schemes, the bio-polymer slurry can actually promote the reactivity of the media.

On some sites, the reactive media can be applied directly to the contamination instead of through a funnel and gate. Usually, these sites have lower groundwater flows and the contamination is less mobile. For these sites, soil mixing provides an ideal method for applying the reactive materials directly without excavation or dewatering. In-situ treatment using soil mixing is usually much less expensive than off-site disposal and completely avoids excavation and transportation costs.

### **2.3 Zinc**

Zinc occurs naturally in air, water and soil, however zinc concentrations are raising unnaturally, this due to addition of zinc through human activities. Most zinc is added during industrial activities, such as mining, electroplating, coal and waste combustion and steel processing.

Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to zinc chloride can cause respiratory disorders.

As mentioned above, the world's zinc production is still rising. This basically means that more and more zinc ends up in the environment. Both surface water and groundwater are contaminated with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants. In addition, zinc is ranked as the second inorganic pollutant in frequency detected in groundwater (USEPA, 1996).

Normally, zinc 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). Battery waste from electronic products is one of major source of zinc. Zinc usually occurs in the +II oxidation state and forms complexes with a number of anions, amino acids and organic acids. Zinc 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). 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 increases as pH increases and salinity decreases.

## 2.4 Natural bentonite

Bentonite is commercially available clay consisting mainly of the clay mineral. The term bentonite indicates a family of clay minerals the structures of which are based on compound layers made up of components with tetrahedral and octahedral coordination. These minerals are found in the form of flat particles that form fine grain aggregates. Chemically, these belong to a specific group of clay minerals: the smectite family, which is characterised by expansibility, by absorption of water and organic molecules within the structural layers, and by considerable cationic exchange properties. The active ingredient in the bentonites is montmorillonite, a hydro silicate of aluminium and magnesium, morphologically composed of octahedral alumina trapped between two layers of tetrahedral silicate.

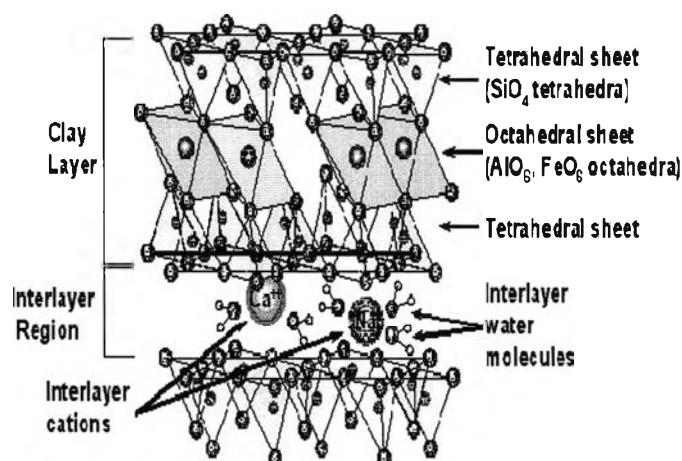


Figure 2.3 Crystalline structure of montmorillonite

The crystalline structure of montmorillonite is shown in figure 2.4. This typical crystalline structure creates an elementary particle of montmorillonite with the characteristic lamella shape. Negative charges are distributed on the external surface of each lamella. The lamellas are held together in packets due to the action of electrostatic forces that build up between the cations ( $\text{Na}^+$ ,  $\text{Ca}^{++}$ ,  $\text{K}^+$ ,  $\text{H}^+$ ) and which can be placed between the lamellas and the negative charge distribution on their surface.

Montmorillonite platelet has a large net negative charge on its surface and a small residual positive charge on the edges due to Van der Waals forces that held the platelets together. This is due to isomorphic substitutions of aluminium ions with magnesium ones and of silica with aluminium. This unbalances the overall platelet charge, leaving a negative charge on the surface. In this case, these negative charges are most frequently neutralized by sodium, calcium or magnesium ions, which are situated in between the platelets or well known as interlayer or exchangeable cations. Due to their stronger positive charge, hydrated calcium ions are tightly bound to the platelet layers and water molecules cannot easily penetrate in between the layers and open them up. This is referred to as calcium bentonite which swells with little or no effect in water. If the interlayer cation is sodium, due to its larger size, water can easily penetrate between the layers and disperse them, giving rise to the typical swelling behavior of the well known sodium bentonites.

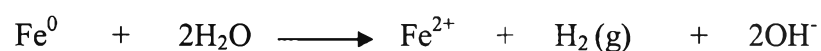
In foundry industries, bentonite is used as one of bonding materials in the preparation of molding sand for the production of iron, steel and non-ferrous casting. The unique properties of bentonite yield green sand moulds with good flowability, compactability and thermal stability for the production of high quality castings.



## 2.5 Zero valence iron

Zero valence iron (ZVI) is often used as a remediation media due to it has a high reduction potential or a strong reducer and is nontoxic and inexpensive (Matheson et al. 1994). The chemical reaction steps with iron occur relatively quickly, however iron does not react quickly with water near neutral pH (Schreier et al. 1994). ZVI is more effective than other metals because the reaction rate of ZVI is limited by mass transport or diffusion (Matheson et al. 1994) while the reaction rate of other metals are limited by the chemistry (Warren et al. 1994). Examples of contaminants that have been treated with zero valence iron are halogenated hydrocarbons, such as carbon tetrachloride and other solvents, nitro aromatics, and heavy metals, such as chromium, mercury. Remediation of metal contaminated sites with an iron metal approach is increasing.

Possible removal reaction mechanisms are similar in that they depend on the surface characteristics of a metal. Direct reaction with iron results in electrochemical reduction of a dissolved metal species is to the zero valence metal onto the iron surface or cementation. This cementation process can be predicted by the standard reduction potentials of the metals (Khudenko et al. 1991). As iron metal corrodes in water, ferrous iron is produced at local anodic sites, and acid is consumed by forming hydrogen gas at local cathodic sites (Stumm et al. 1981). As protons are being consumed from iron corrosion, the concentration of hydroxide increases. The reaction is explained by the following reaction:



Where  $\text{Fe}^0$  is zero valence iron,  $\text{Fe}^{2+}$  is ferrous iron,  $\text{H}_2$  (g) is hydrogen gas, and  $\text{OH}^-$  is hydroxide iron.

Metal hydroxides and hydroxide complexes precipitate when dissolved metals react with hydroxide ions. Metallic atoms and compounds may adsorb to the surface of iron oxides and hydroxides. Dissolved metals may also ion exchange with the iron ions in iron oxides and hydroxides. The ability of a crystal lattice to undergo ion exchange is related to the ionic radius rather than the respective charge of the ions (Shokes and Muller, 1999).

## **2.6 Influence of soil properties on mobility of contaminant**

Physical and chemical properties of the contaminated matrix influence the mobility of metals in soils and groundwater. Contamination exists in three forms in the soil matrix: solubilized contaminants in the soil moisture, adsorbed contaminants on soil surfaces, and contaminants fixed chemically as solid compounds. The physical and chemical properties of the soil will influence the form of the metal contaminant, its mobility, and the technology selected for remediation (Gerber et al., 1991).

### Physical Properties

Particle size distribution can influence the level of metal contamination in a soil. Fine particles ( $<100 \mu\text{m}$ ) are more reactive and have a higher surface area than coarser material. As a result, the fine fraction of a soil often contains the majority of contamination. The distribution of particle sizes with which a metal contaminant is associated can determine the effectiveness of a number of metal remediation technologies, e.g., soil washing (Dzombak et al., 1994).

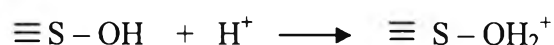
Soil moisture influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water depends on the soil moisture content. Soil structure describes the size, shape, arrangement and degree of development of soils into structural units. Soil structure can influence contaminant mobility by limiting the degree of contact between groundwater and contaminants.

### Chemical Properties

Metal cations are most mobile under acidic conditions while anions tend to sorb to oxide minerals in this pH range (Dzombak and Morel, 1987). 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 (Ellis and Fogg, 1985; Dzombak and Morel, 1987). 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.

### Sorption of heavy metals on metals oxides surfaces

Sorption of metal ions can occur on metal oxide surfaces via surface complexation. The metal oxide surface protonates at low pH:



Where S is a metal of the adsorbing surface and OH is a surface hydroxy group.

When the solution pH is high, the surface hydroxyl group deprotonates:



Therefore, at high solution pH, the surface hydroxyl group can react with metal cations:



Sorption of heavy metals on mineral surfaces is influenced by solute concentrations, surface coverage, and type of metal oxides and pH-dependent. As the solution pH increases, more metal cations are sorbed on the metal oxides due to the negativity charge of the metal oxides (Sparks 1995).

## 2.7 Foundry sand

Waste foundry sand is a by-product from metal casting operations and falls within the definition of waste under the Environment Protection Act (1993). All foundries produce castings by pouring molten metal into molds. Sand casting generates residuals from metal melting and pouring, and molding processes. Residuals consist of spent sand from molding and core-making, slag, and wastes from cleaning rooms, dust collectors or scrubbers. According to the American Foundrymen's Society, 1978, the characteristics of the residuals vary from foundry to foundry, and depend on 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.

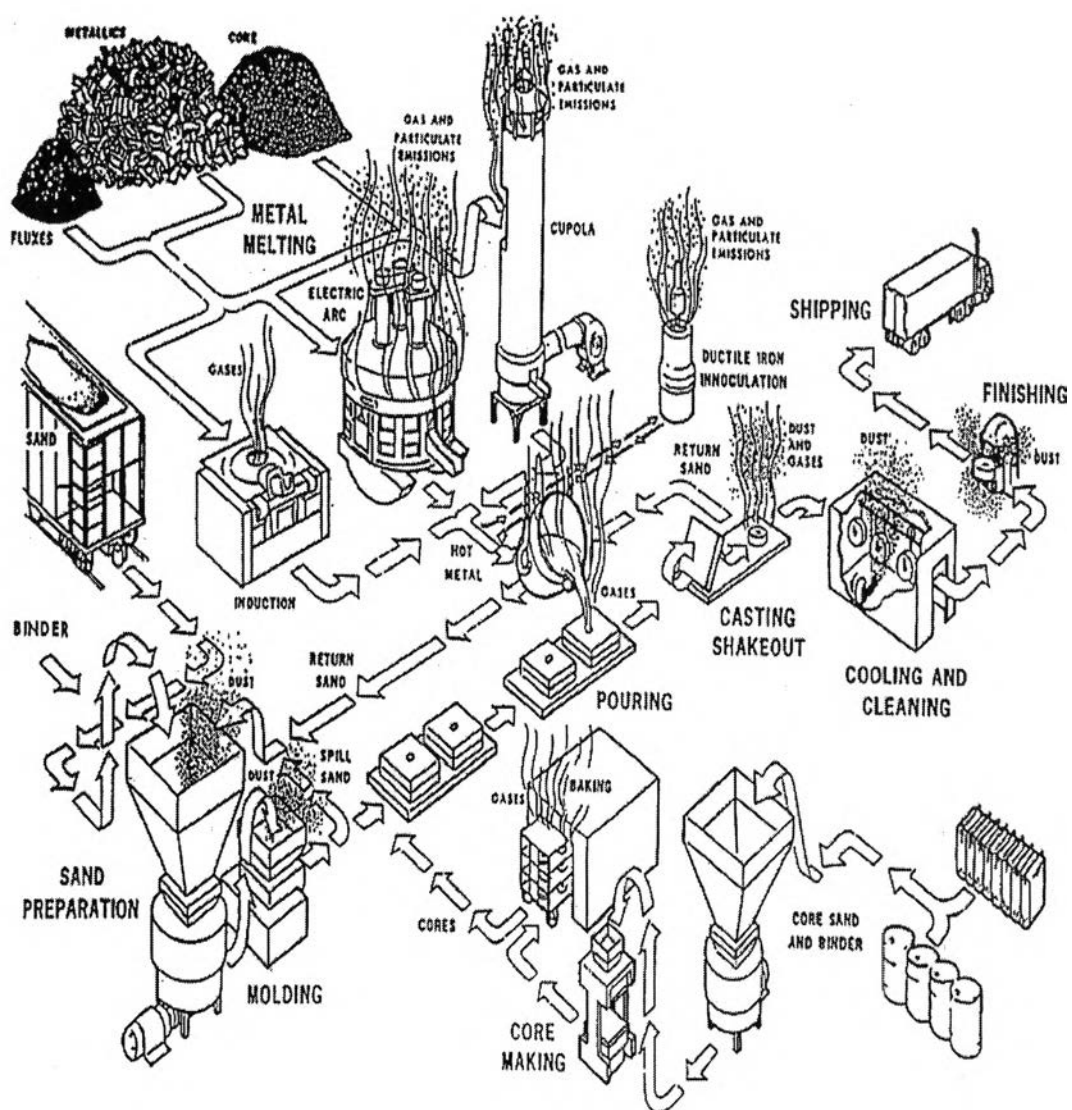


Figure 2.4 Metal casting process (USEPA, 1981)

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 mould ingredient made of finely ground low-sulfur coal that improves casting finish, and up to 4% moisture.

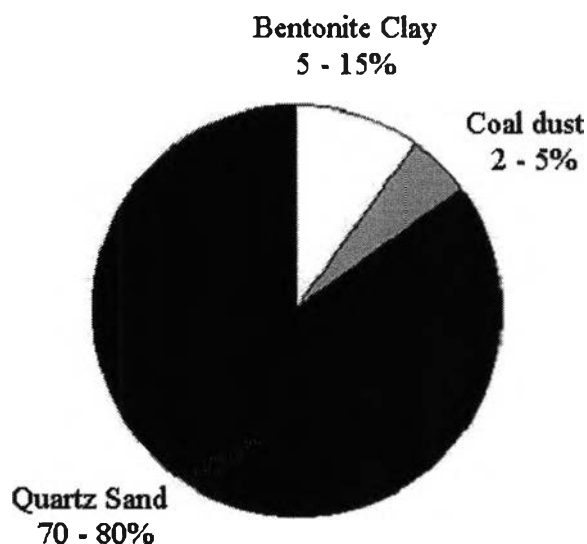


Figure 2.5 Major components of foundry sand

## 2.8 Binder in Foundry sand

Primarily, foundry sand consists of clean, uniformly sized silica sand that is bonded via binders to form molds for ferrous and non-ferrous metal castings. Foundry sand is typically mixed in a specific weight proportion with binder and additive. Foundries employ the use of binders to hold together individual grains of sand that are used to form mold castings. A binder is added to virgin sand, and by means of adhesion or cohesion, bonds sand grains to a degree suitable for metal casting. The two types of binders are clay-bonded and chemically bonded sand. The former is used heavily in iron foundries whereas the latter is used primarily in non-ferrous casting.

### Clay-bonded sand

Clay is a relatively inexpensive and widely available sorbent, which has adsorption capabilities for a variety of metals. Particles smaller than 0.002 mm are classified as clay and have a very large specific surface area, giving them a tremendous capacity to absorb water and other substances. This large adsorptive surface causes clay particles to cohere together in a hard mass after drying. When wet, clay is sticky and can be easily molded.

Clays have been divided into a number of groups according to their structure and composition. The clays used as bonds in synthetic sands, are of four general types (The American Foundrymen's Society, 1978)

1. Fireclays, 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, 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 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, a clay used primarily because of its bleaching qualities closely related to bentonite and used by some as bond clay.
4. Illite, a clay mineral found in many types of clay. However, illite is decomposition product of mica.

The adsorption capabilities of clay result from a net negative charge on the structure of fine-grain silicate minerals. This negative charge is neutralized by the adsorption of positively charged species, giving clay the ability to attract and hold cations such as heavy metals. The large surface area of clays (up to 800 m<sup>2</sup>/g) also contributes to the high adsorption capacity (Cadena et al., 1990). Among the types of clay, montmorillonite clays have the smallest crystals, the largest surface area and the highest cation exchange capacity. Thus montmorillonite clays would be expected to have the highest sorptive capacity (Bailey et al. 1998).

#### Chemically bonded sands

Chemically bonded sands are also used by many foundries in their core making operations. Composition of foundry sand binders and resins is described with respect to their organic compound content. Due to the proprietary nature of foundry sand binders and resins, there is little information regarding the relative proportions of materials used in binder systems. The most common types of binders currently in use include the following: furan or furfuryl alcohol resin, various phenolic urethane resins, alkyd urethane, sodium silicate, phosphate. Other additives include a catalyst to promote the binding process. The majority of chemically bonded systems used in modern foundries are self-setting binders.

### **2.9 Organic addition in foundry sand**

The organic carbon usually acts as a stabilizer that binds inorganic particles. Organic matter can have a dual role: it can reduce metal ion solubility through the binding of metal ions to solid organic matter or increase it through binding to



dissolved organic matter. It is now well established that the free metal ion concentration, which is of relevance in metal bioavailability and toxicity studies, is also often controlled by metal ion binding to natural organic matter.

In the iron foundry, moulds are not usually made only from clay-bonded sand, but one or more of a wide range of organic materials is also added. The nature of the addition depends on whether the mould is to be cast in the process or after drying. The main purposes of additions are as follows:

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

Coal dust is used mainly to improve surface finish and also used more widely than any other material to prevent scabbing. There is a definite improvement in the surface finish of castings when coal dust is added to the moulding sand (Parkes, 1971). The reason of improvement is that when coal dust is poured into and undried mould containing only sand and clay, it found that in certain areas, a layer of sand is so firmly fixed to the casting which cannot be removed by vigorous brushing with a wire brush. It can be shown that the sand is cemented onto casting by a thin layer consisting of silicates, and most of iron and aluminium.

When molten is poured into an undried mould containing sand and moist clay only, the gas present in the pores of the mould is a mixture of air and steam which reacts readily with iron at high temperatures. The exact nature of the reaction products when the iron is liquid and contains 2% of silicon and 3% of carbon is uncertain, however at temperature not too far below the melting point of the metal, iron oxide is formed. The oxide, is chemically active, reacts easily with clay and sand to form mix

silicates with still lower fusion point. When the casting cools, these silicates finally solidify, binding the sand grains to the casting.

By drying the mould, and removing the free water which is partly responsible for the formation of iron oxide, the reaction can be lessened, but it cannot be entirely suppressed since oxygen is still available in reduced amount from the air in the mould pores and the combined water in the clay.

When coal dust is added to the sand, strongly reducing decomposition products fill the mould cavity and the formation of iron oxide is suppressed completely.

Various reasons of adding coal dust to reduce the incidence of scabbing have been put forward; the main effect is that it increases hot plasticity. The coal dust used contain some 30% of volatile matter and most coals of this type partially melt at a temperature of 450°C, 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°C. 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 sands 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.

## 2.10 Beneficial reuse of spent foundry sand

In typical foundry processes, sand from collapsed molds or cores is reclaimed and reused in the casting process. Some new sand and binders are usually added to maintain the quality of the casting and to make up for sand lost during normal operations. However, there is a net loss to the sand system through a sand fraction that is not reclaimable. This spent fraction can be available for beneficial use outside the foundry, in most cases replacing other conventional construction sands or granular materials. However, some foundries with good internal reclamation and sand capture systems, which not only reclaim sand but also reduce its loss through the bag house dust collection systems, dispose at a ratio only 1-2%.

Spent foundry sand is now being actively beneficially used in many countries for example in the U.S.A., Canada, Spain, Japan, New Zealand and others. Some of the various current beneficial use practices are asphalt and other pavers, brick manufacturing, cemetery vaults, hot mix asphalt mixtures, concrete backfill, drainage layers, flowable fill, landfill liners and covers etc.

The by-product mixture of sand and binder has hydraulic properties similar to those of sand-bentonite mixtures that are used as barrier layers throughout the USA (FIRST, 2004). Flowable fill is an ideal application for beneficial use of foundry sand waste because its physical characteristics are similar to those of fine aggregate used in high quality. The spent chemically-bonded casting sand is excellent replacement for portions of the fine aggregate in flowable fill. Roadway structural fill applications provide an opportunity for high volume utilization of excess system sand. Foundry sand can effectively replace conventional materials in hot mix asphalt mixtures by providing at least the same quality. As mentioned above, foundry waste sand is

physically suitable for many applications. Since the major components of foundry sands are sand, clay binder, fine residual iron particles and oxide contents, foundry sands would be expected to have potential as low cost sorbents for alternative beneficial reuse.

Spent foundry sand must possess three qualities to be beneficially used. It must be environmentally benign, i.e., it should not leach metals, alkalis, or organics in amounts that would pose a hazard to human health or the environment under its service condition. It must be economically favorable. And finally, it should be technically equivalent to the material it is replacing in the application. These three factors require a set of definitions acceptable to the industry, regulatory and policy stake holders.

## **2.11 Adsorption isotherms**

Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent (Ho, 1995). The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. There are three major adsorption isotherm equations available from the literature, which are the constant linear model, the Freundlich model and the Langmuir model (Griffin and Shimp 1978; Yong and others 1992; Majone and others 1993; Mohamed and others 1994; Rowe and others 1995). The linear equation holds only at low concentrations of contaminants. At higher concentrations (such as this study), the sorption is always non-linear and more

complex, therefore alternative models such as Freundlich and Langmuir must be used (Rowe and others 1995).

### Langmuir model

Irving Langmuir, an American chemist who was awarded the Nobel Prize for chemistry in 1932, developed a relationship between the amount of gas adsorbed on surface and the pressure of that gas. Such equations are now referred to as Langmuir adsorption isotherms, which is a theoretical adsorption isotherm in the ideal case.

The Langmuir theory was first used to describe the adsorption of gas molecules onto metal surfaces (McKay, 1982). However, this model has found successful application in many other sorption processes. The model assumes that:

1. Adsorption energy is constant and independent of surface coverage;
2. Adsorption occurs at localised sites with no interaction between various ions in the solution;
3. Maximum adsorption occurs when the clay surface is covered by monolayer of cations.

According to the Langmuir model, the amount of zinc adsorbed can be expressed by:

$$q_e = \frac{X}{m} = \frac{Q_0 b C_e}{1 + b C_e}$$

The above equation can be rearranged to the following linear form:

$$\frac{1}{q_e} = \frac{1}{Q_0 b} \cdot \frac{1}{C_e} + \frac{1}{Q_0}$$

The linear form can be used for linearization of experimental data by plotting  $1/q_e$  against  $1/C_e$ . The Langmuir constants  $Q_0$  and  $b$  can be evaluated from the slope and intercept of linear equation.

### Freundlich model

Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm for non ideal systems in 1906. The Freundlich model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of solute adsorbed,  $X/m$ , is related to the concentration of solute in the solution,  $C_e$ , following:

$$\frac{X}{m} = K_f C_e^{1/n}$$

This equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\log \frac{X}{m} = \log K_f + \frac{1}{n} \log C_e$$

Both  $K_f$  and  $n$  are constants, being indicative of the extent of adsorption and the degree of non-linearity between solution and concentration, respectively.

## 2.12 Literature review

The literature on wastewater treatment shows that various types of heavy metals can be removed from aqueous solutions by sorption on oxide surfaces. The mechanisms used in wastewater treatment can also be used in groundwater treatment. Kuan et al. (1998) showed that sand coated with aluminum oxide can remove  $\text{Se}^{4+}$  and  $\text{Se}^{5+}$  from aqueous solution by adsorption. Joshi et al. (1996) conducted sand coated with iron oxide to remove  $\text{As}^{3+}$  and  $\text{As}^{5+}$  via adsorption and co-precipitation.

Clay is a relatively inexpensive and widely available sorbent, which has adsorption capacities for a variety of metals. Due to the smallest crystals, the largest surface area and the highest cation exchange capacity, montmorillonite clays would be expected to have the highest sorptive capacity. A study by Griffin et al. (1977) found the removal of Hg by montmorillonite to be five times greater than that by kaolinite. Viraraghavan and Kopoor (1994) noted that the abundance and low cost of bentonite make it a strong candidate as an adsorbent for the removal of heavy metals from wastewater.

Zinc is a kind of transition metals. The fixation of  $\text{Zn}^{+2}$  by Ca-montmorillonite appears to be controlled by ionic exchange in low ionic strength solution (Auboiroux et al., 1996). Cothenbach et al. (1999) investigated the potential of montmorillonite, Al-montmorillonite and gravel sludge to immobilize zinc ion in agricultural soil. Kraepiel et al. (1999) gave a model for metal ion adsorption on montmorillonite. The sorption of  $\text{Zn}^{+2}$  on Ca-montmorillonite was modeled in terms of cation exchange and surface complexation by Bradbury and Baeyens (1999).

Abollino et al. (2002) investigated the adsorption of heavy metals on Na-montmorillonite. The result showed that the pH variations influenced the

concentrations of Cu, Pb, and Cd in the effluent. Moreover, complex formation hinders the sorption of the metals on the clay with an increasing influence in the order:  $Mn \leq Pb \leq Cd \leq Zn \leq Ni \leq Cu \leq Cr$ .

Zero valence iron has also been shown to successfully treat acidic water contaminated with heavy metals such as chromium, uranium, arsenic, manganese, and zinc (e.g. Cantrell et al., 1999; Shelp et al., 1995; Pule et al., 1999; Shokes and Moller, 1999; Lackovic et al., 2000; Morrison et al., 2002) In most cases, metal removal mechanisms are not well understood but are believed to involve both adsorption and reductive mineral precipitation processes.

Zero-valent iron was used to remove heavy metals by increasing the pH of solution. Reduction by iron metal promoted the removal of cadmium and copper by changing two metals into zero-valent metals. Aluminum, nickel, and zinc were removed slowly by forming hydroxide precipitate (Shokes and Moller, 1999). Moreover, Fe oxide and particulate organic carbon can also remove Pb, Cu, Zn, and Cd by sorption (Paulson 1999).

Wilkin and McNeil (2003) conducted a laboratory study regarding the evaluation of zero-valent iron to treat water impacted by acid mine drainage. Rate of acid-neutralization and of metal (Cu, Cd, Ni, Zn, Hg, Al, and Mn) and metalloid (As) uptake were determined in batch systems using simulated mine drainage. The results indicate that metals removal was the most effective in solutions that were highly undersaturated with respect to pure-metal hydroxides. This suggested that adsorption is the initial and most rapid metal uptake mechanism. Continued adsorption onto or co-precipitation with iron corrosion products are secondary metal uptake processes.



Lee and Benson (2002) conducted batch and column tests to evaluate the potential use of waste foundry sands as an inexpensive medium for zinc removal. The report showed that foundry sands were found to be a good sorbent for zinc. However, the partition coefficient for zinc varies significantly with solution pH. The rate constant for zinc was found to vary within a small limit (typically 0.05-0.20 hr<sup>-1</sup>). Higher rate constants for zinc typically were obtained at higher pH.

Fei Liu et al. (2003) reported that Fe<sup>0</sup> reduces Cr<sup>6+</sup> to Cr<sup>3+</sup> under alkaline and slightly acidic conditions. The removal efficiency rose with an increases in initial concentration of Cr<sup>6+</sup> (1 mg/L to 10 mg/L) when the quantity of Fe<sup>0</sup> is stable. The removal efficiency increased as the quantity of Fe<sup>0</sup> was raised when other conditions are constant. When the initial concentration Cr<sup>6+</sup> is 10 mg/L and pH is 6.5 – 7.7, the final concentration of Cr<sup>6+</sup> in effluent was less than 0.05 mg/L and the total Fe was less than 0.3 mg/L in effluent.