Chapter 2

Review of Literature

2.1 BACKGROUND

The treatment of hazardous wastes using cement based solidification/stabilization technology is of increasing importance. This technology is applied to the wastes which use physical and chemical processes to create chemically stable solids. With the help of this method, the mobility of hazardous substances is drastically reduced in the environment through both physical and chemical means (Kitamura et al. 2002). Generally, this technique involves mixing of wastes with a binder to reduce the leachability. The main object of S/S technique with respect to the remediation of contaminated soil is to achieve and maintain the physical properties and to chemically stabilize or permanently bind contaminants (Connor, 1999). In this chapter, a detailed review of the studies carried out by other researchers on the interactions between cement and heavy metals is presented. Prior to that, a brief literature study was carried out for the adsorption of heavy metal removal from aqueous solution since neem bark powder was used as an additive in the cement matrix to reduce/immobilize Cr$_6^{3+}$ in this research work.

2.2 REVIEW OF LITERATURE ON ADSORPTION OF HEAVY METALS

Contamination due to wastewater poses a serious threat to the environment and human health. Pollution of water resources due to industrial discharges has become a common activity. Rapid population growth, industrialization and urbanization leads indirectly to water scarcity and environmental pollution (Gupta et al. 2012). It is well known that heavy metals like chromium, cadmium, arsenic, nickel, copper and zinc can damage nerves, liver and bones and also interfere with the normal functioning of various metallo-enzymes (Nuhoglu et al. 2002; Ngah et al. 2002; Nourbakhsh et al. 2002; Baik et al. 2002; Saleh and Gupta 2012). Among the heavy metal ions, hexavalent chromium (Cr$_{6}^{3+}$) is recognized as human carcinogen and chronic inhalation increases the risk of lung cancer. It is more hazardous than trivalent chromium (Vieira et al. 2008). Industrial use of Cr$_{6}^{3+}$ compound includes mining, cement, production of steel and metal alloys, electroplating operations, photographic material and corrosive paints (Malkoc et al. 2006). According to the USEPA and BIS standards, the maximum permissible limit of
Cr$_6^+$ discharge into inland surface water is 0.1 mg/L and potable water is 0.05 mg/L respectively. Although different regulatory bodies have set the maximum limits for the discharge of Cr$^{+6}$ in the aquatic systems, toxicity level is being increased in water due to more manufacturing activities.

The excessive use of toxic metals for engineering and its harmful effect upon human health initiates the detection and the removal of heavy metal ions from polluted water and soil. Different electrochemical studies were proposed and used for the detection of heavy metal ions and organic molecules in an aqueous medium (Srivastava et al. 1995; Jain et al. 1995, 1997a,b,2006; Gupta and Kumar 1999; Gupta et al. 1999b, 2002, 2006c, 2007b, 2009a, b; Goyal et al. 2005, 2007a, b, 2008; Singh et al. 2007). Methods like precipitation, oxidation, reduction, coagulation, flocculation, ion exchange, reverse osmosis, membrane separation, electrochemical precipitation-filtration, aerobic & anaerobic treatment, ultra-sonic treatment, photochemical degradation and adsorption (Ali and Gupta 2007; Gupta et al. 2006a, b; 2007a,d,e; 2010a, b; Gupta and Rastogi 2008a; 2009) were used to remove and recover toxic organic & inorganic pollutants from industrial effluents. Among the above mentioned methods, adsorption is regarded as the best for the treatment of water and wastewater in terms of convenience, availability, profitability, design and significant pollutant removal efficiency. Activated carbon is an efficient adsorbent for the removal of heavy metals from domestic and industrial wastewater (Hosea et al. 1986). However, its high cost and loss during the regeneration hampers its applicability (Gupta et al. 2007 b,c). Wide spread use of hazardous chemicals in industries demands the use of inexpensive adsorbents for their removal. Various methods have been developed, that made the production of low cost adsorbents from waste materials possible and obtained significant results (Srivastava et al.1997; Gupta et al. 1997, 2000, 2001; Ali and Gupta 2007). Microbial sources and industrial wastes were also explored for the removal of pollutants from aqueous streams (Gupta et al. 1988, 1999a, 2003, 2010a,b; Gupta and Ali 2000, 2003, 2004; Hamadi 2001; Pehlivan and Arslan 2007; Gupta and Rastogi 2008 a,b,c,d, 2009; Chabaane et al. 2011).

In recent years much attention has been bestowed the use of various low cost agricultural wastes for the removal of toxic pollutants. Waste materials from agricultural sources are widely available and economical. Researchers used agricultural waste
resources like sugarcane bagasse and sugar beet pulp (Sharma and Forster, 1994), (Cimino et al. 2000), pine needles and almond shells (Dakiky et al. 2002), saw dust (Dakiky et al. 2002), hazelnut cactus leaves (Mohanty et al. 2005), coconut tree saw dust (Karthikeyan et al. 2005), eucalyptus bark (Sarin and Pant, 2006), tamarindus indica seed (Agarwal et al. 2006), groundnut husk (Dubey and Gopal, 2007), rice straw (Gao et al. 2008), palm flower (Elangovan et al. 2008), nuts and shell (Pehlivan and Altun, 2008), bael fruit (Anandkumar and Mandal, 2009), saw dust (Naiya et al. 2009), coffee husk (Ahalya et al. 2010), sunflower head (Jain et al. 2010) etc. for the removal of hexavalent chromium. The agricultural materials such as waste tea, turkish coffee, used coffee, hazelnut shells, sugar beet pulps, arjun nuts, etc. have been tried for the removal of other heavy metals also (Cimino et al. 2000; Reddad et al. 2002; Mohanty et al. 2005,). These materials usually composed of lignin and cellulose as the main constituents hence, it has greater affinity for metal complexation. Thus the investigation of their use as adsorbent materials seems to be more appropriate.

Recently, a great deal of interest in the research for the removal of heavy metals from industrial effluent has been focused on the use of agricultural by-products as adsorbents. The use of agricultural by-products in bioremediation of heavy metal ions, is known as bio-sorption. This utilizes inactive (non-living) microbial biomass to bind and concentrate heavy metals from waste streams by purely physico-chemical pathways (mainly chelation and adsorption) of uptake (Igwe et al. 2005). New resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk can be used as an adsorbent for heavy metal uptake after chemical modification or conversion by heating into activated carbon. Ajmal et al. (2000) employed orange peel for Ni(II) removal from simulated wastewater. They found that the maximum metal removal occurred at pH 6.0. The applicability of coconut shell charcoal (CSC) modified with oxidizing agents and/or chitosan for Cr(VI) removal was investigated by Babel and Kurniawan (2004). Cu(II) and Zn(II) removal from real wastewater were studied using pecan shells-activated carbon (Bansode et al. 2003) and potato peels charcoal (Amana et al. 2008). Bishnoi et al. (2003) conducted a study on Cr(VI) removal by rice husk-activated carbon from an aqueous solution. They found that the maximum metal removal by rice husk took place at pH 2.0. Rice hull, containing cellulose, lignin, carbohydrate and silica, was investigated for
Cr(VI) removal from simulated solution (Tang et al. 2003). To enhance its metal removal, the adsorbent was modified with ethylenediamine. The maximum Cr(VI) adsorption of 23.4 mg/g was reported to take place at pH 2.

In this work, a non-conventional finely ground (90µm) Neem Bark Powder (NBP) has been used as an adsorbent for the removal of hexavalent chromium from aqueous solutions and used as an additive in S/S technique to reduce/immobilize the same toxic metal. The neem tree is native to Southeast Asia and grows in many countries throughout the world (Ascher, 1993). It is widely used in many industries like herbal, agricultural, oral care, cosmetic, tanning and dyeing industries. In addition, it has more life span and faster growth which make it unique when compared to other trees.

2.3 REVIEW OF LITERATURE ON S/S TECHNIQUE

The main aim of the cement-based solidification/stabilization (S/S) is to either bind or complex the compounds of a hazardous waste stream into a stable insoluble form (stabilization) or to trap the waste within a solid cementitious matrix (solidification) (Wiles, 1987). The U.S. Environmental Protection Agency (EPA) has recognized S/S as the best demonstrated available technology for 57 RCRA (Resource Conservation and Recovery Act)-listed hazardous wastes. (U.S. EPA 2004). When compared with other available remediation technologies, cement-based S/S has the following advantages (Conner and Hoeffner, 1998; Shi and Spence, 2004):

- Comparatively low cost and ease of use and handing,
- Composition of portland cement is consistent from source to source,
- Significantly efficient in long-term stability, both physically and chemically,
- Satisfying impact and compressive strength,
- Non-toxicity of the chemical compounds,
- High resistance to biodegradation, and
- Relatively low water permeability.

Stabilization of heavy metals is mainly achieved by converting the heavy metals into insoluble precipitates. Organic compounds are generally nonpolar and hydrophobic; they do not react with the inorganic binders and may interfere with the hydration reactions of cement or pozzolanic materials and inhibit the setting of cement. Instead, organics are
generally sorbed or encapsulated in the pores, and their leachability depends on their solubility in water and their diffusivity through the waste matrix. In S/S processes, immobilization of contaminants, depending on their nature, occurs by three main mechanisms:

1. Chemical fixation of contaminants by interactions between the hydration products of cement and the contaminants,
2. Physical adsorption of contaminants on the surface of cement hydration products, or
3. Physical encapsulation of contaminated waste or soil.

2.4 MECHANISM OF SOIL CEMENT STABILISATION

The fundamental mechanism of soil cement stabilization was outlined by Lea (1970). The components of Portland cement are tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminates (C₃A) and tetracalcium alumina-ferrite (C₄A). These four main constituents are the major strength producing components. When the pore water of the soil comes into contact with cement, hydration reaction of cement occurs rapidly and primary cementitious products, namely hydrated calcium silicates (C₂SHₓ, C₃S₂Hₓ), hydrated calcium aluminates (C₃AHₓ, C₄AHₓ) and hydrated lime Ca(OH) are formed. The first two cementitious products are the primary cementitious products whilst the hydrated lime is deposited as a separate crystalline solid phase. The cement particles bind the adjacent cement grains together during hardening and form a hardened skeleton matrix, which encloses unaltered soil particles. In addition, the hydration of cement leads to the rise of pH of the pore water, which is caused by the dissociation of the hydrated lime. The strong bases react with the soil silica and alumina (which are inherently acidic) both from the clay minerals and amorphous materials on the clay particles surfaces, in a manner similar to the reaction between a weak acid and a strong base. The hydrous silica and alumina will then gradually react with the calcium ions liberated from the hydrolysis of cement to form insoluble compounds (secondary cementitious products), which hardens when cured to stabilize the soil. This secondary reaction is known as the pozzolanic reaction. The reactions that take place in soil–cement stabilization can be represented in the following equations; the reactions given here are for tricalcium silicate (C₃S) only, because it is the most important constituents of Portland cement (Lea, 1970).
Major Product of Cement
\[ C_3S + H_2O \rightarrow C_3S_2H_x \text{ (Hydrated Gel)} + \text{Ca(OH)}_2 \]  
(2.1)

Derived Product of Cement
\[ \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2(\text{OH})^- \]  
(2.2)

\[ \text{Ca}^{2+} + 2(\text{OH})^- + \text{SiO}_2 \text{ (Soil Silica)} \rightarrow \text{C-S-H} \]  
(2.3)

Derived Product of Cement
\[ \text{Ca}^{2+} + 2(\text{OH})^- + \text{Al}_2\text{O}_3 \text{ (Soil Alumina)} \rightarrow \text{C-A-H} \]  
(2.4)

2.5 FACTORS INFLUENCING SOLIDIFICATION/STABILISATION

The most important admixtures in cement–based solidification/stabilization are gypsum, calcium chloride, sodium carbonate, calcium hydroxide, carbon dioxide, and activated carbon (Conner, 1999). Hence, in addition to the phase composition and structure, the reaction rates of cement phases are variable and dependent on temperature, particle shape and size, and the presence of accelerators or retarding agents as stated by Ortego and Jackson (1989), Hills et al. (1994), and Hills and Pollard (1997). There are other important factors which can affect the cement hardening, according to Glasser (1997); due to the fact that the larger surface area available for hydration, more hydration products form at early ages with higher initial strength. This is related to the effect of fineness on the rate of hardening of cement. In addition, other factors that affect the setting rate and diffusion of soluble constituents from the interior into the inter-particle space after solidification like particle size and shape of cement grains. Furthermore, degree of cement hydration, reaction rates and products of cement hydration can be affected by temperature. The transport of species in solidified waste is influenced by temperature which leads expansion or shrinkage of solidified waste. Hence, if the temperature exceeds 60-70 °C, serious loss of durability can occur (Kiellsen, 1996; Escalante and Sharp, 1998a, 1998b, and 1999). As mentioned by Zhang and Odler (1996) and Scrivener et al. (1999) about aluminate effect, it may cause undesirably rapid setting when it reacts rapidly with water, and also may cause undesirable properties of some products formed (e.g., hexagonal C-A-H). In addition, Calcium sulphate, gypsum (CaSO$_4$.2H$_2$O) or its analogues such as bassanite (CaSO$_4$.5H$_2$O) or anhydrite CaSO$_4$ (including its polymorphic forms $\alpha$- and $\gamma$-CaSO$_4$) is added as a set-controlling agent of
aluminate. Furthermore, if the sulphate is present in high concentrations, that cause destructive expansion from reaction with sulphates.

Other vital factors were also reported by Dweck and Buchler (2000), Dweck et al. (2003), Hill and Sharp (2002), and Abderlraxig et al. (1999). One of the most important factors is that calcium oxides influence the thermodynamics and kinetics of C-S-H formation. It also affects the morphological and structural features of C-S-H. The other factor, calcium hydroxide which is consuming process such as carbonation or the displacement of solubility equilibrium of portlandit (e.g., change of temperature, addition of calcium salts or alkalis) might change the characteristics of C-S-H. On the other hand, as stated by Glasser (1997), other alkali compounds accelerate the rate of early hydration of cement and give higher early compressive strength, although the final strength is lower than that of the low alkali cement. While in the presence the alkalis with gypsum, some phases such as \((\text{C}_4\text{A}_0.9\text{SO}_4).1.1\text{N}0.5\text{H}_{16}\) will form and may cause deleterious effects, in particular, causing expansion. Another typical accelerator factor is calcium chloride, it can reduce the setting time and double early compressive strength, in spite of the final strength may be reduced. But in the presence of calcium chloride with gypsum, new phase produce like Kuzel’s salt \((\text{C}_3\text{A}.0.5\text{CaCl}_2.0.5\text{CaSO}_4.10\text{H}_2\text{O})\) or Friedel’s salt \((\text{C}_3\text{A}.\text{CaCl}_2.12\text{H}_2\text{O})\) may form depending on the activity of those species in solution (Glasser et al. 1999). According to Cocke and Mollah (1993) and Spence and Shi (2004), organic is one of the factors affected on cement hydration. It can exhibit an affinity towards cement particles or cement hydration products by adsorption due to the electrostatic force, hydrogen-bonding interaction, chemical bonding, and hydrophobic force. Therefore, adsorbed organics will alter surface properties of the cement particles and thus its interaction with the solution as well as with other cement particles. Also, they may interfere with the bonding of wastes with cement binders leading to decrease in unconfined compressive strength and impair short-term or long–term durability (Chen et al. 2009).
2.6 HYDRATION OF CEMENT AND IMMOBILIZATION OF HEAVY METALS

The hydration of cement is a sequence of overlapping chemical reaction between cement clinker compounds, calcium sulphate and water, leading to continuous cement paste stiffening and hardening (Chen et al. 2009). The early behaviour of hydrating cement is governed by reactions of aluminate phases; the setting and early strength development behavior is mostly dependent on the hydration of silicates, particularly alite. The formation of hydration products and the development of micro-structural features depend on solution process, interfacial reactions and, ultimately, solid-state reaction (Macphee et al. 1989; Scrivener et al. 1999; Gore and Milestone, 2007). The hydration products of portland cement comprise approximately 20-25% Ca(OH)$_2$, 60-70% C-S-H and 5-15% other phases, including grains of still-anhydrite cement. It has been proposed that hydration of cement can be divided into five stages, as shown in Table 2.1 (Taylor, 1997).

As mentioned by Tashiro et al. (1979), hydration of cement can be modified by heavy metals due to coating around cement grains. According to Poon et al. (1985) and Poon et al. (1986), metals that form the least soluble hydroxide retard hydration reactions; those that form more soluble hydroxides exhibit only a slight degree of retardation; and metals forming soluble hydroxides behave as acceleration of cement hydration. Retardation has been attributed to the reduction in permeability caused by these reaction products, which is the precipitation of insoluble metal colloidal gels on cement grain surface.

2.6.1 INFLUENCE OF ADDITIVES ON CEMENT HYDRATION

Most of the development work on stabilization of hazardous contaminants was done before 1990. Portland cement-based processes remain the most common, and many different additives are being used to improve performance and reduce the cost with specific waste streams (Conner and Hoeffner, 1998). Table 2.2 shows the types of additives used in S/S processes.
Table 2.1 Hydration kinetics of cement

<table>
<thead>
<tr>
<th>Phase</th>
<th>Outcome</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial stage</td>
<td>Wetting of surface, dissolution phases, ettringite nucleation</td>
<td>Up to 15 minutes</td>
</tr>
<tr>
<td>Induction stage</td>
<td>Development of ettringite needles and C-S-H gels precipitation</td>
<td>From 15 minutes to 4 hours</td>
</tr>
<tr>
<td>Accelerating stage</td>
<td>Effect of osmotic pressure on protective layer</td>
<td>From 4 to 8 hours</td>
</tr>
<tr>
<td>Decelerating and hardening</td>
<td>Transformation of AFt into AFm</td>
<td>From 8 to 24 hours</td>
</tr>
<tr>
<td>stage</td>
<td>Additional hydration</td>
<td>After 24 hours</td>
</tr>
</tbody>
</table>

2.6.1.1 Inorganic additives

The effects of soluble inorganic salt on hydration of C₃S have been studied thoroughly by Kantro (1975). The efficiency of hydration acceleration of different cations are found to be Ca²⁺ > Mg²⁺ > Sr²⁺ > Ba²⁺ ~ Li⁺ > K⁺ > Rb⁺ ~ Cs⁺ > Na⁺ > NR⁴⁺ > H₂O where NR⁴⁺ denotes quaternary ammonium ion and H₂O denotes the absence of additive. In most cases, an accelerated rate of hydration, i.e., shortened setting time, would increase the rate of early strength development. The results indicate that (i) calcium has the highest efficiency and (ii) the efficiency mainly depends on the charge and size of the ion, with small, highly charged ions being the most effective. For the highly soluble salts of calcium at the same equivalent concentration, the order of effectiveness of anions is Br⁻ > Cl⁻ > SCN⁻ > I⁻ > NO₃⁻ > ClO₄⁻ > H₂O, which shows a similar trend as that of cations in terms of ion size. The salts of Zn, Sn, Pb, soluble phosphates, and fluorides retard the hydration process, and inorganic salts which form complexes with calcium also act as retarders.

2.6.1.2 Organic additives

Almost all organic compounds are retarders in cement setting, and many organic acids that strongly chelate calcium also have strong retarding capability. Organic compounds retard the cement setting process by forming a protective layer around the cement grain, thus hindering the formation of calcium hydroxide (Chandra and Foldin, 1987; Edmeades and Hewlett, 1998; Montgomery et al. 1991a; Sora et al. 2002). Organic
alcohols such as methanol and phenol not only retard the hydration process, but also form amorphous structures after drying, resulting in detrimental effects on the compressive strength of the cement (Sora et al. 2002). It is reported that phenol retards the initial and final setting times of cement by hindering the normal hydration reactions and by preventing the formation of calcium hydroxide during the initial period of setting and hardening (Vipulanandan and Krishnan, 1993). 3-Chlorophenol interferes with the hydration of cement by stabilizing ettringite formation and delaying its conversion to monosulfate (Pollard et al. 1991). In general, the mechanisms of retardation by organic compounds include: (i) formation of insoluble calcium compounds, (ii) adsorption, and (iii) complexation.

2.7 STANDARD TESTING METHODS

This section describes the suitability of commonly used standard test methods for characterizing the properties of a soil-cement specimen, including hydraulic conductivity and leaching behaviour. In designing a cement-based S/S treatment for contaminated soil, these tests are mainly used in treatability studies to compare the laboratory performance of different cement mixes. However, it must be emphasized that there are no regulations requiring any particular test, and the set of parameters to be tested is usually selected by the technology vendor based on various factors such as soil characteristics, location of the contaminated site, method of treatment implementation, and the subsequent use of the remediated site.

2.7.1 HYDRAULIC CONDUCTIVITY

Permeability, also referred to as hydraulic conductivity, of a solidified/stabilized material is an important parameter, as it provides a measure of how easy the water can pass through the material. More importantly, when considered in conjunction with leaching test results, it allows assessment of a solidified/stabilized material with respect to its ability to retain contaminants. Permeability can be measured in the laboratory using two methods: (i) constant-head and (ii) falling-head (U.S. EPA, 1986). In the constant-head method, water is allowed to flow through the sample under a constant liquid pressure (head) on both sides of the sample.
Table 2.2 Types of additives used in Solidification/Stabilisation processes. (Source: Conner and Hoeffner, 1998)

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Types of additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Activated carbon</td>
</tr>
<tr>
<td>2</td>
<td>Carbonates</td>
</tr>
<tr>
<td>3</td>
<td>Concrete additives</td>
</tr>
<tr>
<td>4</td>
<td>Iron and aluminum compounds</td>
</tr>
<tr>
<td>5</td>
<td>Neutralizing agents</td>
</tr>
<tr>
<td>6</td>
<td>Organophilic clays</td>
</tr>
<tr>
<td>7</td>
<td>Phosphates</td>
</tr>
<tr>
<td>8</td>
<td>Reducing agents</td>
</tr>
<tr>
<td>9</td>
<td>Rubber particulates</td>
</tr>
<tr>
<td>10</td>
<td>Silica fume</td>
</tr>
<tr>
<td>11</td>
<td>Slag</td>
</tr>
<tr>
<td>12</td>
<td>Soluble silicates</td>
</tr>
<tr>
<td>13</td>
<td>Sorbents (fly ash, clays, minerals etc)</td>
</tr>
<tr>
<td>14</td>
<td>Sulfides (Organic and inorganic)</td>
</tr>
<tr>
<td>15</td>
<td>Surfactants</td>
</tr>
<tr>
<td>16</td>
<td>Organic latex</td>
</tr>
</tbody>
</table>

The permeability can then be related to system parameters such as pressure gradient and water flow rate using Darcy’s law, after the flow rate at the outlet (usually maintained at atmospheric pressure) has reached a constant value. The constant-head method is suitable for samples with high permeability (> $10^{-6}$ cm/s) (U.S. EPA, 1989).

2.7.2 LEACHING

In the context of S/S, leaching is defined as the process of gradual extraction of contaminants from treated wastes through exposure to either stagnant or flowing of leachant (in the form of water or other solvent) through and around the wastes. The following paragraph describes the leaching mechanisms pertaining to S/S-treated waste in the presence of a leachant. A stabilized waste is a porous solid which is at least partially saturated by water and gas. There may be several different solid phases, each containing contaminants. Prior to introduction of leachant, this pore system is in equilibrium with
the surrounding solid phase and therefore, there is no net transfer between phases. The leachant alters the composition of the system and disrupts the chemical equilibrium, resulting in the mobilization of contaminants. The new system may evolve towards a new equilibrium if sufficient time passes with no leachant renewal. At this stage, the two basic leaching mechanisms are mobilization and transport of the contaminant. The leachant mobilizes contaminants within the pores by dissolving the contaminant while dissolution results from a combination of chemical and physical mechanisms. Factors that affect the extent of equilibrium concentrations include the solubility of constituent and chemical makeup of the pore water. As more soluble constituents are leached from a relatively insoluble solid matrix, a layer deficient in the leached constituents develops. As constituents leach, the layer may become more porous compared to the unleached solid, so that molecular diffusion in the pore water and boundary layer phenomena become the limiting factors. Transport of the mobilized contaminants occurs by bulk advective flow or diffusion. If water flows within the S/S-treated waste, advective transport causes contaminants that have been mobilized by reactions in the pores to flow through the waste. Figure 2.1 illustrates the various leaching mechanisms that pertain to S/S-treated waste.

Fig. 2.1 Leaching mechanism

2.7.2.1 Toxicity Characteristic Leaching Procedure

This test is a single-extraction batch test. The waste S/S specimens are crushed to a particle size smaller than 9.5 mm. Two choices of buffered acidic extraction fluids (acetic acids) are offered under TCLP, depending on the alkalinity and the buffering
capacity of the wastes. Extraction fluid # 1 has a pH of 4.93 ± 0.05 and extraction fluid # 2 has a pH of 2.88 ± 0.05. The extraction fluid is added to a zero head space extractor (ZHE) at a liquid-to-solid ratio of 20:1, and the sample is agitated with a National Bureau of Standards (NBS) rotary tumbler for 18 hours. The liquid solution is filtered through a 0.6 to 0.8 µm borosilicate glass filter under 50 psi pressure for analysis.

2.7.2.2 Semi-dynamic leaching test (ANS 16.1)

In addition to TCLP and SPLP, semi-dynamic leaching tests can also be used to determine the leaching behaviour of contaminants out of a cement-solidified material. Unlike TCLP or SPLP, where the samples are crushed into small particles, an intact sample is used in the semi-dynamic leaching test. Several specimen geometries (cylinder, parallelepiped, or sphere) and dimensions can be used, but the cylindrical shape is preferred. The procedure specifies the leachant replacement intervals, and the cumulative fraction (CFR) of a substance released during the test is measured. Assuming a constant effective diffusion coefficient $D_e$, the CFR can be calculated (Dutré et al. 1998). In addition to the standard test method described above, other test procedures, particularly for contaminant leaching, have also been developed for cement-based S/S treated wastes (Sanchez et al. 2000; van der Sloot and Dijkstra, 2004; Barna et al. 2005). A database of test data from the literature (“MONOLITH”) has also been developed, with an objective of developing models to examine correlations within the data set and predict properties of cement-based S/S materials (Perera et al. 2005).

2.8 CHROMIUM REDOX CHEMISTRY

Chromium has wide range of oxidation states (from -2 to +6), but only the +3 and +6 states are stable under most conditions. As a common rule, Cr$^6+$ is expected to to predominate in highly oxygenated drinking water or when strong oxidants such as chlorine or moderately strong oxidants like chloramines are present in water. At low Cr concentrations in typical drinking water conditions (Figure 2.2), Cr(VI) is present as monovalent HCrO$_4^-$ below pH 6.5 and divalent CrO$_4^{2-}$ between pH 6.5 to 10. At very low or no oxygen levels, Cr(III) is the dominant species, which will be in cationic (Cr$^{3+}$, CrOH$^{+2}$, or Cr(OH)$_2^+$) or neutral (Cr(OH)$_3^0$) form depending on the pH. Cr(III) tends to be extremely insoluble (< 20 µg/L) between pH 7 and pH 10, with minimum solubility at pH 8 of about 1 µg/L (Rai et al, 1987).
2.9 SOLIDIFICATION / STABILIZATION OF INORGANIC CONTAMINANTS

Cement-based S/S has been used extensively with inorganic solid wastes which contain heavy metals such as As, Cd, Cr, Cu, Ni, Pb, and Zn (Bhatty et al. 1999), and numerous experimental and modeling studies can be found in literature (Islam et al. 2004a, b; Catalan et al. 2002; Stegemann and Buenfeld, 2002; Stegemann and Buenfeld, 2003). These processes are usually categorized based on the type of additives through which solidification is achieved (Sharma and Lewis, 1994):

- Cement based
- Pozzolan based
- Thermoplastic method
- Organic polymerization method
- Encapsulation method
- Organophilic-clay based

Each technique has certain advantages and disadvantages. Cement-based and pozzolan-based techniques are preferred over the others mainly because of their low material and equipment cost while having good solidification characteristics at the same time. Some metals such as arsenic(III), chromium(VI), and mercury are not suitable for use with this type of treatment since they do not form highly insoluble hydroxides (Mulligan et al. 2001). The formation of insoluble hydroxides is an important aspect of cement-based S/S technology. The solubility of Cd, Cr, Cu, Pb, Ni, and Zn hydroxides decreases with increasing pH up to a value of about 10 (Cullinane et al. 1986; Shi and
Spence, 2004). Above this pH, the solubility increases with pH as the metal cations form soluble complex anions with excess hydroxide ions. Indeed, the variation of metal hydroxide solubility with pH is an important factor for the S/S process because the pore solution of hydrated cement paste is highly alkaline (pH ≈ 13) (Mollah et al. 1995).

2.9.1 ARSENIC

Arsenic (As) is known to be a toxic element and a carcinogen to humans (Mollah et al. 1998); even trace amounts of arsenic can be harmful to human health (Karim, 2000). In recent years, arsenic has caused great public concern due to the increased awareness of the health risks associated with consumption of arsenic-containing water. The U.S. EPA reduced the maximum concentration level (MCL) of arsenic in drinking water from 50 to 10 µg/L in January 2001 (Federal Register, 2001). In nature, arsenics are present in two valence states, As(III) and As(V) (Boyle and Jonasson, 1973), with As(III) being both mobile and toxic (Boyle and Jonasson, 1973; Pantsar-Kallio and Manninen, 1997). Indeed, As(III) is 25–60 times more toxic than As(V) (Dutré and Vandecasteele, 1995a; Corwin et al. 1999). Another source of As is the waste fly ash from the metallurgical industry. It was also used extensively for agricultural applications such as herbicides and insecticides (Leist et al. 2000). Several researchers have shown that arsenic can be immobilized using S/S technology. To improve the immobilization efficiency of arsenic, many researchers have used other additives with Portland cement. In general, the primary purposes for using additives are: (i) oxidation of As(III) to As(IV), because As(IV) can form low leachable compound and (ii) formation of stable complex with calcium or iron. Many researchers have shown that, in the presence of lime, arsenic immobilization is mainly due to the formation of Ca-As precipitates. For example, the formation of Ca₃(AsO₄)₂ and CaHAsO₃ precipitates is the main mechanism of immobilization of As in contaminated soils that have been treated with cement, lime, and pozzolanic material (Dutré and Vandecasteele, 1995a, 1998; Dutré et al. 1999; Vandecasteele et al. 2002). In the presence of lime at high pH (12–13), the precipitation reactions can be written as

\[
\begin{align*}
\text{As}_2\text{O}_5 + 3\text{Ca(OH)}_2 & \xrightarrow{\text{pH-12-13}} \text{Ca}_3(\text{AsO}_4)_2 \downarrow + 2\text{H}_2\text{O} \\
\text{As}_2\text{O}_3 + 2\text{Ca(OH)}_2 & \xrightarrow{\text{pH-12-13}} 2\text{CaHAsO}_3 \downarrow + \text{H}_2\text{O}
\end{align*}
\]
Bothe and Brown (1999) suggested that lime addition reduces As mobility in contaminated slurries due to the formation of low-solubility Ca-As precipitates such as Ca₄(OH)₂(AsO₄)₂·4H₂O and Ca₅(AsO₄)₃(OH). The effectiveness of both As(III) and As(V) immobilization can be enhanced by increasing the Ca/As molar ratio. More specifically, Moon et al. (2004) found a significant increase in As(III) immobilization at Ca/As molar ratios greater than 1:1, and similar observation was made for As(V) at Ca/As molar ratios greater than or equal to 2.5:1. A different compound, NaCaAsO₄·7.5H₂O, was reported when As(V) reacted with cement-lime-kaolinite or cement-fly ash (Moon et al. 2004; Akhter et al. 1997). The efficiency of arsenic immobilization can also be improved with iron salt (Voight et al. 1996; Miller et al. 2000; Fuessle and Taylor, 2004a, b; Jing et al. 2003). Fuessle and Taylor (2000) suggested that Fe(II) is generally preferable for arsenic S/S because it is effective over a wide range of mixing ratios and over the long term. The use of Fe(III) is not recommended for arsenate S/S since fresh cement mix adsorbs ferric ion and does not allow adequate S/S until after a long cure time. Furthermore, the ferric hydroxy-arsenic complex is a larger molecule than the ferrous arsenic compound, which makes encapsulation by the cement matrix more difficult. Miller et al. (2000) showed that leaching was reduced when the soil was pretreated with FeSO₄, then with Portland cement (7 days after), rather than mixing Portland cement and FeSO₄ together. Since it is well known that As(V) can be immobilized more easily than As(III) with cement, many researchers have attempted the oxidation of As(III) to As(V) using H₂O₂ before S/S treatment for better performance (Dutré et al. 1999; Palfy et al. 1999; Vandecasteele et al. 2002; Fuessle and Taylor, 2000).

2.9.2 CADMIUM

A natural source of cadmium (Cd) comes from volcanic activities, which can release Cd into the atmosphere, spreading it over a wide area (Mulligan et al. 2001). In the past twenty years, cadmium has become a concern due to its extensive use in industrial applications such as steel plating, pigment stabilization, and nickel-cadmium batteries. Excessive accumulation of cadmium is associated with various toxic effects in human, including renal dysfunction and osteomalacia (Burgatsacaze et al. 1996). Cadmium is more mobile at lower pH (4.5–5.5) and less mobile above pH 7.5. Fuessle
and Taylor (2004b) have studied the effect of aging of cement matrix on the leaching characteristic of cadmium. They found low Cd concentration in TCLP extracts when the curing time of the cement matrix was short, and the concentration increased when the curing time was more than one year. This phenomenon may be attributed to pH variation. Cadmium hydroxide has the lowest solubility at about pH 11. With the short aging time, the extract pH was between 10 and 12 for two mix designs, suggesting a low solubility for cadmium hydroxide. The importance of pH has also been reported by other researchers (Halim et al. 2003, 2004; Coz et al. 2004). In particular, high cadmium concentrations were found in the leachate when the leachate pH was below 5, which is consistent with the study described above. In addition, based on an analysis of the cementitious structure, it was also found that Cd(OH)$_2$ precipitates are not homogeneously distributed in the C-S-H matrix. Rather, they are concentrated within the cement pores or adsorbed on the C-S-H matrix, with up to 30% concentrated at various other locations. Shokes and Moller (1999) also reported that colloidal iron could reduce the mobility of cadmium.

### 2.9.3 COPPER

Copper (Cu) is found naturally in sandstones and in minerals such as malachite and chalcopyrite. Increased levels of copper in soil are due to uses in fertilizers, pesticide sprays, building materials, rayon manufacture, agricultural and municipal wastes, and industrial emissions. Polettini et al. (2004) reported the immobilization of copper in cement using an agglomeration agent, sodium metasilicate (Na$_2$SiO$_3$.9H$_2$O). In their study, two phases, copper hydroxide (Cu(OH)$_2$) and atacamite (Cu$_2$(OH)$_3$Cl), were identified as candidates for controlling copper solubility in leachate solution. Copper hydroxide was the controlling phase at pH values higher than 7, while atacamite became the solubility-controlling solid under acidic conditions. They showed that the predominant immobilization mechanism for copper was related to the precipitation/dissolution phenomena and was strongly dependent on the pH of the leachate solution. Copper can also be effectively immobilized using cement based, lime based (Yukselen and Alpaslan, 2001; Fatta et al. 2004), and natural zeolite like clinoptilolite (Balkan and Kocasoy, 2004) based solidification/stabilization treatment.
Zain et al. (2004) have shown that the waste copper slag from blasting operation can be safely solidified and stabilized in a cement-based system.

2.9.4 NICKEL

There are many studies on the S/S treatment of Nickel (Ni) with Portland cement (Roy et al. 1992, 1993; Fatta et al. 2004; Fuessle and Taylor, 2004b), cement-fly ash (Roy et al. 1993), and cement-zeolite mixture (Shanableh and Kharabsheh, 1996; Balkan and Kocasoy, 2004). Roy et al. (1992) observed that hydration of Portland cement was retarded by Ni-containing sludge, but the hydration products are the same as those formed without Ni. Physical encapsulation of metal hydroxide by cement was the principal mechanism of stabilization.

2.9.5 LEAD

Lead (Pb) is found naturally in soils, most commonly in the form of ore galena (PbS) and in smaller quantities in cerussite (PbCO₃), anglesite (PbSO₄) and crocoite (PbCrO₄). Sources of lead contaminants include lead-zinc smelters, piping, insecticides, paints, and batteries. Lead concentration in leachate after solidification/stabilization by Portland cement has been found to be dependent primarily on the leachate pH (Yukselen and Alpaslan, 2001; Alpaslan and Yukselen, 2002; Halim et al. 2003; Fuessle and Taylor, 2004b). In particular, Pb concentration in leachate decreases with increasing pH. It becomes undetectable when the pH is between 9 and 11 due to the formation of insoluble hydroxide, but is again detectable at pH 12 due to the formation of amphoteric Pb hydroxide complexes. It was suggested that the mechanism of Pb immobilization involves not only a physical encapsulation mechanism, but also the formation of a new phase with Al and Si-rich species. Using X-ray analysis, Halim et al. (2004) found that Pb was evenly distributed throughout the C-S-H of cementitious matrix, which supports the notion that Pb immobilization is not only due to physical encapsulation.

2.9.6 ZINC

Sources of zinc (Zn) in soil include brass and bronze alloys, galvanized products, cosmetics, pharmaceuticals, batteries, metal coatings, glass, paint, and zinc-based alloys. Zinc is commonly found in waste as zinc chloride, zinc oxide, zinc sulfate and zinc sulfide. Zinc hydrolyzes at pH 7.0–7.5, forming Zn(OH)₂ at pH above 8 (Mulligan et al. 2001). Under anoxic conditions, ZnS can form ZnOH⁺, ZnCO₃ and ZnCl⁺. In a study
using cement and binder, Coz et al. (2004) showed that zinc concentration in the leachate under a wide range of pH was very similar to that calculated based on the solubility of the hydroxide ions. In addition, the hydroxyl complexes Zn(OH)$_4^{2-}$ and Zn(OH)$_5^{2-}$ can also be present in a strong alkaline solution (Li et al. 2001). Their anionic properties preclude their adsorption onto the negative surface of C-S-H, but they may form calcium zinc complex hydrated compound such as CaZn$_2$(OH)$_6$·H$_2$O (Mollah et al. 1992).

**2.9.7 CHROMIUM**

The effects of chromium (Cr) on different Portland cement phases and the solidification of Cr in cementitious matrices have been studied by various researchers (Stephan et al. 1999a; Omotoso et al. 1996; Vallejo et al. 1999; Park 2000; Trezza and Ferraiuolo, 2003; Fatta et al. 2004; Halim et al. 2004; Polettini et al. 2004). The solidification of chromium can be related to the formation of Ca-Cr aluminates and the formation of phases such as Ca$_4$Al$_6$O$_{12}$CrO$_4$ and Ca$_6$Al$_4$Cr$_2$O$_5$ (Stephan et al. 1999b). Some authors consider that the ettringite phase is also involved in this mechanism by the substitution of Al by Cr(III) and/or SO$_4^{2-}$ by CrO$_4^{2-}$, since modified Cr-ettringite, CaO·Al$_2$O$_3$·3CaCrO$_4$·32H$_2$O, was observed in the XRD study by Macias et al. (1997). Trezza and Ferraiuolo (2003) studied the properties of limestone-blended (20%) cement in the presence of Cr(VI) and showed that (i) hydration was retarded and the compressive strength was reduced, especially at early ages, and (ii) leaching test result was similar to that of ordinary Portland cement at neutral pH, but Portland cement performed better at acidic pH (3). Vallejo et al. (1999) have reported the stabilization of Cr(III) with 20% Portland cement and 3% Depocrete SM/2 (a type of cement which cures very rapidly) as a stabilizer. The appearances of calcium chromium silicate, aluminium chromium oxide hydroxide and calcium dichromate was found in the XRD study by Lin et al (1997). Though the coexistence of Cr$^{2+}$ and Cr$^{6+}$ is very unlikely, it would provide a possible mechanism for the immobilization of chromium in cement matrices. The probable substitution of Cr for Si and the interaction among Cr, Si and Al in the hydrated Portland cement may enter into C-S-H. Wang and Vipulanandan (2000) solidified Cr$^{6+}$ with cement. As the cement content was high, formation of CaCrO$_4$ was more. The solubility of CaCrO$_4$ is 5.1 x 10$^{-6}$. Obviously, leaching was not observed in their study.
2.10 IMMOBILIZATION MECHANISM OF HEAVY METALS

The possible immobilization mechanisms of heavy metals could be (1) sorption, (2) chemical incorporation (surface complexation, precipitation, co-precipitation, diodochy), and (3) microencapsulation (Chen et al. 2009; Trussel and Spence, 1994; Glasser, 1997). As stated by Tamas et al. (1992) and Cheng and Bishop (1998), there are two products for sorption of heavy metals on cement hydration; physical adsorption and chemical adsorption. Physical adsorption happens when contaminants in the solution (pore water) are attracted to the surface of particles because of unsatisfied charges of the particles while the phenomena of chemical adsorption generally occurs through covalent bonding which refers to high affinity and specific adsorption. Many factors led to modify the binding capacity of hydration products of cement for toxic metals like the surface charges, chemical reaction involving surface functional groups and specifically adsorbed ions. Kitamura et al. (2002) reported the precipitation mechanisms of heavy metals as follows: “In the precipitation of cement hydration products, heavy metal ions may be adsorbed on their surfaces and then enter the lattice to form a solid solution, altering their structures (crystallinity, particle size) and solubility.” The chemical precipitation is the dominant fixation mechanism for heavy metals in most cases of cement-based s/s system. According to Cannell et al. (2000) and Sulhan et al. (2003), the heavy metals saturation compounds are usually very high and that lead to homogenous or spontaneous nucleation for these compounds occurs very quickly. If it takes into account the heterogeneous nucleation and secondary nucleation, the nucleation time could be even shorter. Furthermore, the structure with the highest entropy develops first and then transforms to more stable crystalline phases subsequently depending on the Ostwald’s rule. As reported by Hills et al. (1994), James (1996), and Conner and Hoeffiner (1998) heavy metals can be precipitated as hydroxides, carbonates, sulphates and silicates in cement-based s/s systems. When the pH of a solution of dissolved metal ions is raised to some optimum level for a specific metal, hydroxide precipitation occurs. The optimum pH is different for each metal and for different valence states of a single metal.