CHAPTER II

BACKGROUNDS AND LITERATURE REVIEW

This research is importance to study the theory, concept, and literature review as follow:

2.1 Sugar Production
2.2 Lead and Chromium
2.3 Theory of Adsorption
2.4 Theory of Reduction of Cr(VI)
2.5 Portland Cement
2.6 Solidification and Stabilization (S/S) Process
2.7 Concrete Blocks

2.1 Sugar Production

Sugarcane is an ephemeral herb belonging to the grass family that is native to tropical and subtropical regions of the world like Thailand. This tropical grass has pointed leaves, 10-24 feet in height, and several stalks. The segmented stalks have a bud at each joint and as the plant matures, small flowers appear. Mature sugarcanes are cut at ground level. Removed the leaves and trimmed off the top by cutting off the last mature joint. Then place the sugarcane into large piles and picked up, tied, and transported to a sugar factory. (Chetthamrongchai, et al., 2001)

2.1.1 Sugar Industry in Thailand

Demand form domestic and international markets have been rising and have contributed to the economic growth of the nation. Sugar cane growing and processing into raw sugar is one of the largest industries in the country. Thailand is one of the largest sugar exporters in the world. The total export of white and raw sugar was 3.22 million tons in 2000. The Office of the Cane and Sugar Board under the Ministry of Industry has reported the total value of sugar exports for the crop-year 1998-1999 at 21.21 billion baht and total sales of sugar cane of nearly 24 billion baht for the crop 1999-2000 (Chetthamrongchai, et al., 2001).

2.1.2 Sugar Production Process

Sugar production process summarizes form Chansakran (1999), Chetthamrongchai, et al. (2001), and Jarutawai (2002) that follow:

1. Grinding: A machine led by a series of rotating knives, shreds the sugarcane into pieces. During grinding, hot water is sprayed on to the sugarcane to dissolve any remaining hard sugar. The smaller pieces of sugarcane are spread out on a conveyer belt.

2. Milling: The shredded pieces of sugarcane pass through a series of heavy-duty rollers by conveyer. The juice is extracted from the pulp.

3. Clarifying: Use the milk of a lime added to the liquid sugar mixture. Then heat them to the boiling point. The calcium carbonate is form when the carbon dioxide travels through the liquid. It attracts non-sugar debris such as fats, gums, and wax from the juice. And remove them from the sugar juice in a clarifier tank.

4. Evaporation: Boil the clear juice under a vacuum and low temperature. It is heated until it forms into a thick and brown syrup. In this process can remove water about 75%.

5. Crystallization: The little water is left in the sugar syrup by evaporating and generated crystallization. Inside a sterilized vacuum pan, pulverized sugar is fed into the pan and then formation of crystals. The remaining mixture is a thick mass of large

crystals which is sent to a centrifuge to spin and dry the crystals. The dried product is raw sugar which still inedible.

6. Refinery or Purification: Transport the raw sugar to a refinery process for the removal molasses, minerals and other non-sugar which still contaminate in sugar. Raw sugar is mixed with a solution of sugar and water to loosen the molasses from the outside of the raw sugar crystals, producing a thick matter known as magma. Separate the molasses from the crystals by filter under high pressure or spin. Crystals are washed, dissolved and filtered to remove impurities. The golden syrup which is produced and then sent through resin filters to remove the color and water. The concentrated and clear syrup are generated and then fed it into a vacuum pan again. Sugar production process was shown in Figure 2.1.

2.1.3 Waste form Sugar Factory

Bagasse and bagasse fly ash for this research was collected from Saraburi Sugar Co., Ltd. in the province of Saraburi, Thailand. Byproducts of the factory are bagasse, filter cake, and molasses. All of them are utilized in many activities. The filter cake is generated about 3 % of total sugar cane input and used as fertilizer. While, molasses is generated about 5 % of total sugar cane input and used as raw material for brewery, MSG, citric acid, ethanol, and animal feed industry. The major portion, bagasse is generated at about 30 % of total sugar cane input and used as fuel for boilers (shown in Figure 2.1) to generate steam and electricity for the factory. Excess electricity is sold to Electricity Generating Authority of Thailand (EGAT). The factory has bagasse fly ash management as shown in Figure 2.2. Bagasse and bagasse fly ash are generated in large amount. As a result, they still create waste management problem for the factory.

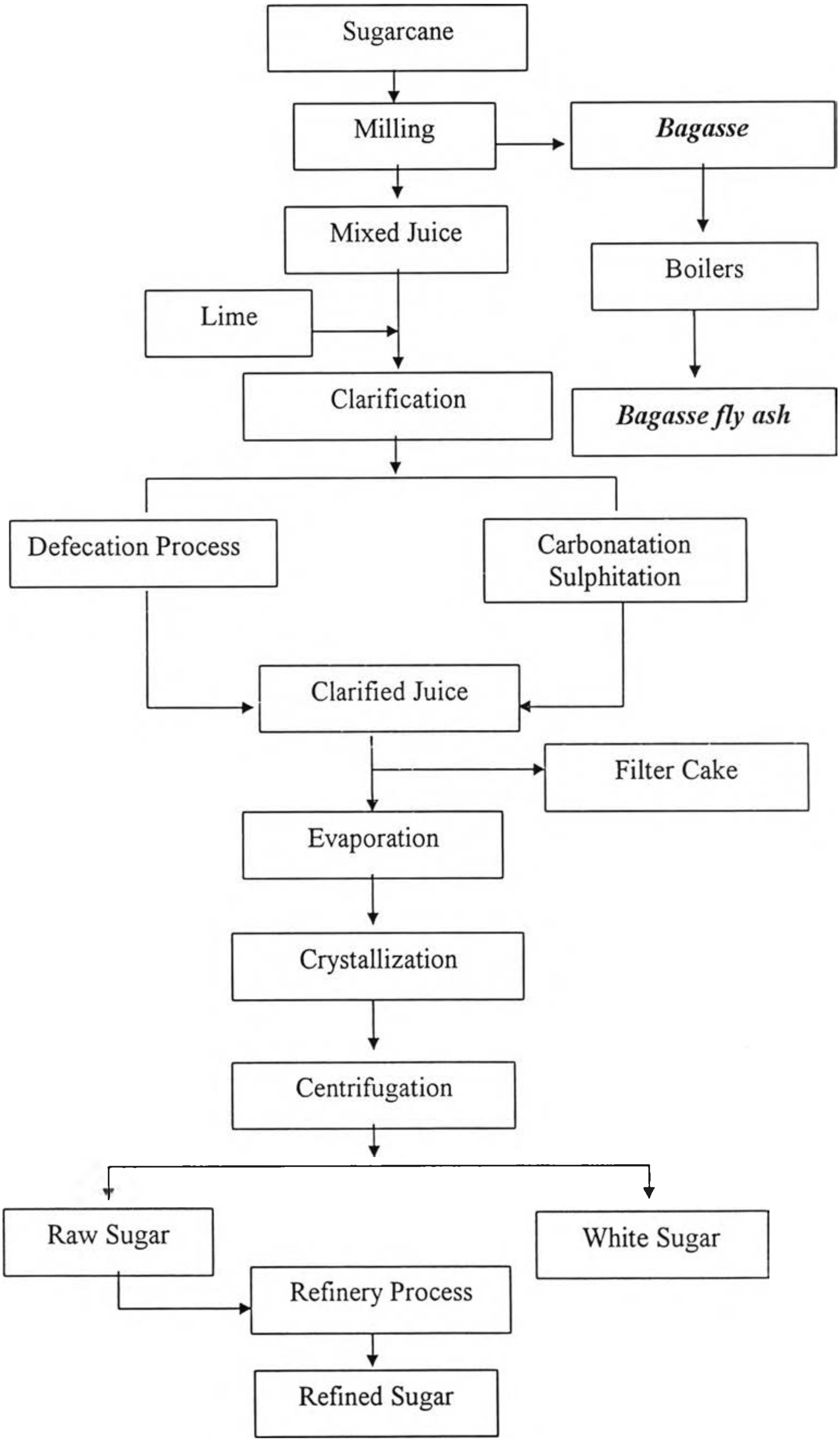


Figure 2.1 Process of Sugar Production (adapted from Jarutawai, 2002)

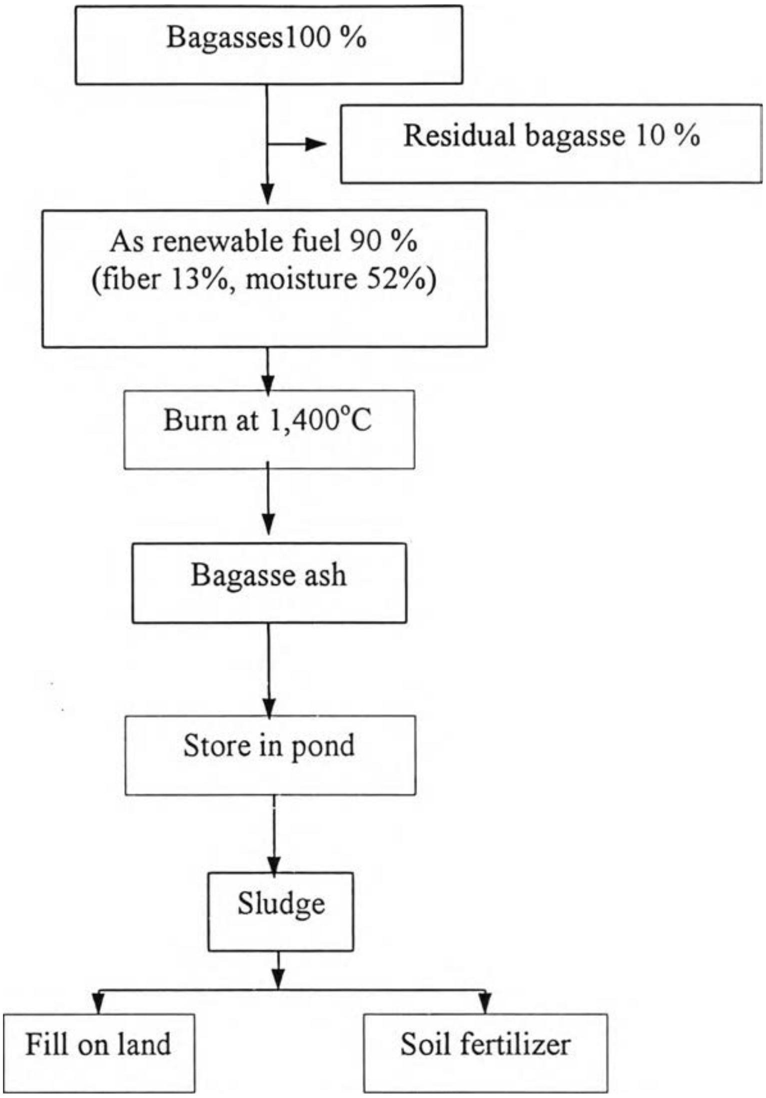


Figure 2.2 Process of Bagasse Management (adapted from Jarutawai, 2002)

2.1.4 Characteristic of Waste form Sugar Factory

Gupta and Ali (2000) studied characteristic of bagasse fly ash collected from a local sugar factory at Iqbalpur, (U.P.), India. They found that it was stable in water, dilute acids and bases. The oxide composition of the bagasse fly ash was SiO_2 = 60.5%, Al_2O_3 = 15.4%, CaO = 2.90%, Fe_2O_3 = 4.90%, and MgO = 0.81%. The loss on ignition was found to be 16.00% by weight. The density and porosity were 1.01

g/cm^3 and 0.36 fractions, respectively. The surface area of particle size 200-250 μm was 450 m^2/g. Compared with Portland Cement, it consist of main oxides, SiO_2 (17-25%), Al_2O_3 (3-8%), CaO (60-67%), Fe_2O_3 (0.5-6.0%), and sub oxide such as MgO (0.1-5.5%).

Katyal, Thambimuthu, and Valix (2003) reported that bagasse contained about 45-50% moisture, 43-52% fiber, and 2-6% soluble solids. The typical composition of bagasse fiber was about 26.6-54.3% cellulose, 22.3-29.7% hemicellulose, and 14.3-24.45% lignin. Bagasse is characterized as a low-density fiber and by its wide particle size distribution (less than 100 μm to grater than 10 cm).

Kosayothin (2002) reported that the chemical compositions of bagasse are analyzed using dry weight. The bagasse consists of fiber and soluble substance. The fiber contains 44-45% of cellulose, 25% of pentosan, 20% of lignin, and 10% of other.

2.2 Lead and Chromium

Lead and chromium are heavy metals. The term, heavy metal, is used loosely to refer to almost any metal with an atomic number higher than that of calcium (20). The basic information, usefulness in manufacture, adverse effect, and treatment of lead and chromium is show in Table 2.1.

Sorption is the dominant mechanism controlling the distribution of lead in the aquatic environment. Lead solubility is very low (< 1 g/L at pH 8.5-11) in water containing carbon dioxide and sulfate. At constant pH, the solubility of lead decreases with increasing alkalinity. Lead is not very mobile under normal environmental conditions. It is retained in the upper 2.5 cm of soil, especially soils with at least 5 % organic matter of a pH of 5 or above. Predominance diagrams in aqueous solution of lead species show in Figure 2.3. The solubility of Pb is 10 μg/L above pH 8, while near pH 6.5 the solubility can exceed 100 μg/L (Cotton, et al., 1999).

In natural waters, dissolved chromium exists as either Cr(III) cations or in anions such as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), where it is hexavalent with oxidation number +6. It generally is present at low concentrations in natural waters. Predominance diagrams in aqueous solution of Cr(VI) species, for chromium concentration of $7*10^{-4}$ M, is shown in Figure 2.4. Background levels in water typically range between 0.2-20 µg/L, with an average of 1 µg/L. The hexavalent form of chromium, existing in negatively charged complexes, is not sorbed to any extent by soil or particulate matter and is much more mobile than Cr(III). However, Cr(VI) is a strong oxidant and reacts readily with any oxidizable organic material present (Eisler, 2000).

Table 2.1 Information of Lead and Chromium

Name	**Lead**	**Chromium**
Basic information		
Symbol	Pb	Cr
Atomic Number	82	24
Atomic Radius	175 pm	129 pm
Atomic Mass (amu)	207.17	51.9964
Melting Point	327.4 °C (600.55 K, 649.9 °F)	1857.0 °C (2130.15 K, 3374.6 °F)
Boiling Point	1755.0 °C (2028.15 K, 3216.6 °F)	2672.0 °C (2945.15 K, 4841.6 °F)
Number of Protons	82	24
Number of Neutrons	125	28
Classification	transition metal	transition metal
Density at 293 K	11.35 g/cm^3	7.19 g/cm^3
Color	gray	gray
Valence states	Zero, two and four	Zero to six
Predominant form	Pb(II)	Cr(III) and Cr(VI)

Table 2.1 (Cont.)

Name	**Lead**	**Chromium**
Natural sources		
	Weathering of minerals Particularly galena	Weathering of rocks and soil
Usefulness in manufacturing		
	Make grids, connectors, and terminals in storage batteries	Alloys
	Pigments	Electroplating
	Glass colorizers	Dyes and paint pigments
	Heat stabilizers in plastics	Preservation of wood
	Mining, milling and smelting of Pb and metals associated with Pb	Leather tanning
	Electroplating	Corrosion inhibitor (cooling tower)
	Construction materials	Protective coating on metals
	Ceramics	Decorative and wear-resistant
	dyes	catalysts
	Radiation and cable shielding	Magnetic taps
	Ammunition	Cement
	Paints	Paper
	Glassware	Floor covering
	Solder and piping	rubber
Adverse effect		
Chronic exposure	Cancer, damage the blood forming, nervous, urinary and reproductive systems	Cancer, mutation, damage to the liver, kidney circulatory, and nerve tissues, dermatitis

Table 2.1 (Cont.)

Name	Lead	Chromium
Acute exposure	Acute encephalopathy (brain disease) may progress to seizure, coma and death from cardiovascular arrest	Skin irritation and ulceration
Treatment	Precipitation, solvent extraction, ion exchange, and adsorption on activated carbon	Precipitation, solvent extraction, ion exchange, and adsorption on activated carbon
Drinking water standards	zero	0.1 mg/L (total Cr)
Effluent standards	< 0.2 mg/L	Cr (III) < 0.75 mg/L Cr(IV) < 0.25 mg/L

Notation: collected from Jones and Atkins, 2002; Cotton, et al., 1999; Eister, 2000; Landis and Yu, 1999.

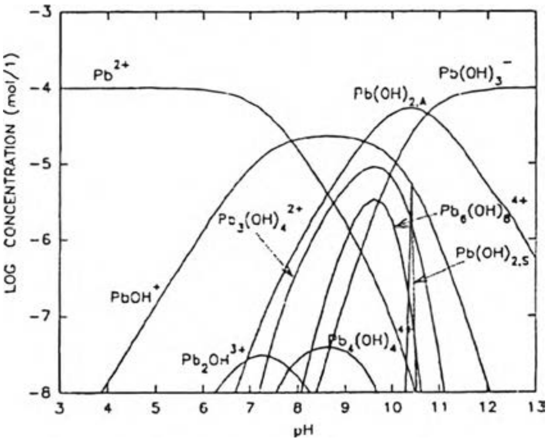


Figure 2.3 Predominance Diagrams in Aqueous Solution of Lead Species (Herreta-Urbina and Fuerstenau, 1995)

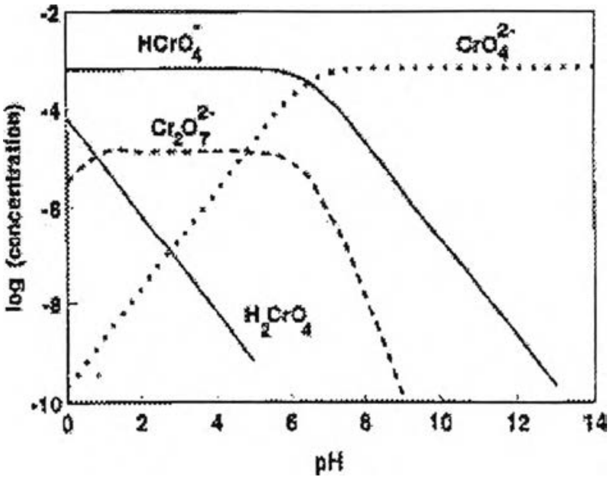


Figure 2.4 Predominance Diagrams in Aqueous Solution of Cr(VI) Species, for Chromium Concentration of $7*10^{-4}$ M. (Gimenez, et al., 1996)

2.3 Theory of Adsorption

Adsorption is the physical and/or chemical process that substance is accumulated at an interface between phases. Adsorption involves the interphase accumulation or concentration of substances at a surface of interface. The process can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. The material being concentrated of adsorbed is the adsorbate, and the adsorbing phase is termed the adsorbent (Weber, 1972).

For the purposes of water treatment, adsorption from solution occurs when impurities in the water accumulate at a solid-liquid interface. The adsorbent is the solid phase that the accumulation occurs and adsorbate is the substance being removed from the liquid phase to the interface. In the process of adsorption may be classified as physical and/or chemical force. The physical adsorption is the van der Waals forces and dispersion force, while chemical adsorption includes the transfer of electron and formation of chemical bonding. The surface charge on the adsorbent can adsorb the opposite charge. This condition is similar to the ion exchange process (Ruangchainikom, 2002 and Kanokporn, 2002).

2.3.1 Adsorption Mechanism

The removal of heavy metal by adsorptive process involves the steps (Weber, 1972; Ruangchainikom, 2002; and Kanokporn, 2002) as follow:

2.3.1.1 Adsorptive Transport: The molecules are transported from solution to the boundary layer of water surrounding adsorbent. This transport occurs by water transportation or turbulent mixing.

2.3.1.2 Film Diffusion Transport: The adsorbates are transported by molecular diffusion through the layer of water that surrounds the adsorbent particles.

2.3.1.3 Pore Diffusion Transport: The adsorbent has many pores in the particles. After passing through the film of water, the adsorbates are transported through the adsorbent's pore to available adsorptive sites.

2.3.1.4 Adsorptive Process: After transport to an available site, the adsorptive bond is formed between the adsorbate and adsorbent. This reaction is occurred by physical adsorption that is very rapid. However, it can be occurred by chemical reaction that is slower than the diffusion reaction.

2.3.2 Rate of Adsorption

There are three consecutive steps in the adsorption of materials from solution by porous adsorbents (Chermisinoff, 1978) as follow:

2.3.2.1 The transport of the adsorbate through a surface film to the exterior of the adsorbent.

2.3.2.2 Sorption by porous adsorbents.

2.3.2.3 Adsorption of the solute on the interior surfaces bounding the pore and capillary spaces of the adsorbent.

2.3.4 Types of Adsorbents

There are three types of adsorbents (American Water Works Association, 1990) as follow:

2.3.4.1 Inorganic substances: There have the surface density about 50-200 m^2/g. For example, magnesium oxide, bone char, and activated carbon, etc. Activated carbon can adsorb ions better than the other inorganic substance. The surface density is about 600-1,000 m^2/g. Although the activated carbon can be regenerated and reused, the regeneration of activated carbon must use of high temperature and expensive operation cost.

2.3.4.2 Organic substance: It produced from natural material such as bark, fiber, shell, and peel, etc. It has a functional group for the adsorption of opposite ions similar to the synthetic resin.

2.3.4.3 Synthetic resin: It has functional groups that have been used for the adsorption of opposite ions. A fell resins are called macroporous resin of adsorbent resin such as styrene divinylbenzene (SDVB) resin and phenol-formaldehyde (PF) resin. The surface density is about 300-500 m^2/g that less that the activated carbon. However, the synthetic resin can be regenerated and lower operation cost than the activated carbon.

2.3.5 Factors Influencing Adsorption

There are six factors influencing adsorption (Weber, 1972; Chermisinoff, 1978; Ruangchainikom, 2002; and Kanokporn, 2002) as follow:

2.3.5.1 Surface Area

Adsorption is a surface phenomenon; the extent of adsorption is proportional to specific surface area. The extent of a surface reaction will vary with available surface area, adsorption rate should exhibit a monotocic increase with some function of the inverse of the diameter of the adsorbent particles. If the mechanism of uptake is one of adsorption on external sites of a nonporous adsorbent, the rate should vary reciprocally with the first power of the diameter for a given mass of adsorbent. This inverse relationship holds also for porous adsorbents when the rate of transport to internal surface areas is controlled by an external resistance. Conversely, for cases in which intra-particle transport controls the sorption rate, the variation should be with the reciprocal of some higher power of the diameter.

2.3.5.2 Nature of the Adsorbate

The solubility of the solute is, to a large extent, a controlling factor for adsorption equilibria. A general rule for prediction of the effect of solute polarity on adsorption is that a polar solute will prefer the phase which is more polar. In other words, a polar solute will be strongly adsorbed from a nonpolar solvent by a polar adsorbent, but will much prefer a polar solvent to a nonpolar adsorbent.

2.3.5.3 pH

The pH of a solution may influence the extent of adsorption. Because hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions in influenced by the pH of the solution. Furthermore, to the extent to which the ionization of an acidic or basic compound affects its adsorption, pH affects adsorption in that it governs the degree of ionization.

2.3.5.4 Temperature

Adsorption reactions are normally exothermic: thus the extent of adsorption generally increases with decreasing temperature. The changes in enthalpy for adsorption are usually of the order of those for condensation of crystallization reactions. Thus small variations in temperature tend not to alter the adsorption process to a significant extent.

2.3.5.5 Adsorption of Mixed Solutes

In the application of adsorption for purification of waters and wastewaters the material to be adsorbed commonly will be a mixture of many compounds rather than a single one. The compounds may mutually enhance adsorption, may act relatively independently, or may interfere with one another. Mutual inhibition of adsorption capacity can be predicted to occur provided: adsorption is confined to a single or a few molecular layers; the adsorption affinities of the solutes do not differ by several orders of magnitude; and there is not a specific interaction between solutes enhancing adsorption. Similarly, because the adsorption of one substance will tend to reduce the number of open sites, hence the concentration of adsorbent available as a driving force to produce adsorption of the other substance, mutually depressing effects on rates of adsorption may be predicted.

2.3.5.6 Nature of the Adsorbent

The physicochemical nature of the adsorbent can have profound effects on both rate and capacity for adsorption. Every solid is a potential adsorbent, but consideration of the surface character of every type of solid material is outside the scope or the present discussion.

2.3.6 Adsorption Isotherm

An isotherm is the relationship that shows the distribution of adsorbate (material adsorbed) between adsorbed phase (that adsorbed on the surface of the adsorbent) and solution phase at equilibrium. There are divided to two types 1) GAC Isotherms and 2) Polymeric, Clay, Zeolite, Molecular Sieve Isotherms. Only the GAC Isotherms will be used in this research.

Isotherms are generally recognized mathematical relationships developed to describe the equilibrium distribution of a solute between the dissolved (liquid) and adsorbed (solid) phased. These relationships help interpret the adsorption data obtained during constant temperature tests, referred to as adsorption isotherms. There are divided into three types as follows:

2.3.6.1 Langmuir isotherm has been used by many workers to study sorption of a variety of compounds (Gupta and Ali, 2001). The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface (Gupta and Ali, 2001). The Langmuir isotherm relationship is of a hyperbolic form as shown in Equation 2.1. The Langmuir relationship can be linearized by plotting ether 1/q vs $1/C_e$. The linear form of the Langmuir isotherm is given by Equation 2.2.

$$q = Q_o \, b \, C_e / (1+b \, C_e) \qquad 2.1)$$

$$1/q = 1/Q_o + 1/b \, Q_o \, C_e \qquad 2.2)$$

Where: q is the amount of sorbate adsorbed per unit weight of adsorbents and C_e is the equilibrium concentration of the adsorbate (mg/L). Langmuir constants, Q_o and b are related to maximum adsorption capacity and energy of adsorption through the Arrhenius equation, respectively. Q_o can also be interpreted as the total number of binding sites that are available for sorption. When m/x or 1/q is plotted against $1/C_e$, a straight line with slope $1/b \, Q_o$ is obtained and intercept is correspond to $1/Q_o$.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor, r, which describes the type of isotherm and is defined by Equation 2.3)

$$r = 1/(1+b\,C_o) \qquad 2.3)$$

Where: b is a Langmuir constant and C_o is the initial concentration of sorbate (Gupta and Ali, 2000).

If,		
	$r > 1$	unfavorable
	$r = 1$	linear
	$0 < r < 1$	favorable
	$r = 0$	irreversible

2.3.6.2 The Brunauer, Emmet, and Teller (BET) equation also assumes that the adsorbent surface is composed of fixed individual sites. However, the BET equation assumes that molecules can be adsorbed more than one layer thick on the surface of the adsorbent. The BET equation assumes that the energy required to adsorb the first particle layer is adequate to hold the monolayer in place.

2.3.6.3 The Fruendlich isotherm equation assumes that the adsorbent has a heterogeneous surface composed of adsorption site with different adsorption potentials. The Freundlich isotherm relationship is exponential, given by the Equation 2.4). The linear form of the Langmuir isotherm is given by Equation 2.5).

$$Q = K_f\,C_e^{(1/n)} \qquad 2.4)$$

$$\log q = \log K_f + 1/n \log C_e \qquad 2.5)$$

where K_f and n are the Freundlich constants that are associated with adsorption capacity and adsorption intensity, respectively. The value of n between 2 and 10 shows good adsorption (Nassem and Tahir, 2001). The other parameters have been defined as in equation 2.1) and 2.2). A plot of log q against log C_e gives a straight line, the slope and intercept of which correspond to 1/n and log K_f, respectively (Gupta and Ali, 2001).

2.3.7 Bagasse and Bagasse Fly Ash as Adsorbent for Heavy Metal Removal

Bagasse supplies fuel for the generation of steam in sugar factories. However, most factories have an excess of bagasse during regular grinding season. Lignin from sugarcane bagasse, can adsorb heavy metals. **Peternele et al. (1999)** studied adsorption of **Cd(II)** and **Pb(II)** onto functionalized formic lignin form sugarcane bagasse. They studied the effects of temperature, pH and ionic strength on adsorption of Cd(II) and Pb(II) onto carboxymethylated lignin form sugarcane bagasse. Sugarcane bagasse was extracted sequentially with *n*-hexane, ethanol, and water in a soxhlet system. The sample obtained was air dried and then added formic acid to pre-extract and heated until reflux, when HCl was added to obtain a 1% solution. After 3 h in reflux, filtered and washed sample with concentrated formic acid and concentrated at reduced pressure until a viscous liquid was formed. This liquid was poured on cooled water and precipitated lignin was obtained. The result showed that the adsorptions were fitted to the Langmuir model. The most important variables are temperature and ionic strength for the Pb(II) adsorption in single and binary system, respectively. For both metals, maximum binding capacity decreased with the ionic strength increase. Increasing pH the Pb(II) adsorption is enhanced. Carboxymethylated lignin adsorbed Pb(II) selectively at pH 6.0, 30°C and 0.1 mol/dm of ionic strength.

In recent years, many researchers have focused their interests on production of low-cost adsorbents instead of activated carbon, which remains an expensive material. Bagasse fly ash, a waste generated form the sugar industry, many researchers successfully used wastes of several prime industries to remove metals and other toxic substances. The developed adsorbents were very useful, economic, and reproducible for the removal toxic substances. **Gupta and Ali (2000)** investigated to utilization of bagasse fly ash (a sugar industry waste) for the removal of **copper** and **zinc** from wastewater. They varied pH, adsorbent dose, initial metal ion concentration, temperature, and particle size and tested in batch and column experiment. These researchers had found that the adsorption reaction was endothermic and followed Langmuir and Freundlich model. Copper and zinc were sorbed by the developed adsorbent up to 90-95% at a pH of 4.0 for copper and 5.0 for zinc with and adsorbent of particle size 200-250 μm, and dose of 10 g/l. The equilibrium was attained in 60 and 75 min for copper and zinc, respectively. The removal of these two metal ions was achieved up to 93-98% in column experiments at a flow rate of 0.50 ml/min.

Some researches studied the comparison of efficiency between bagasse and fly ash to remove heavy metals. **Rao, Parwate, and Bhole (2002)** studied removal of **Cr^{6+}** and **Ni^{2+}** from aqueous solution using raw bagasse and fly ash. They pretreated raw bagasse with 0.1N NaOH and 0.1N CH_3COOH. The batch experiment, studied effect of hydrogen ion concentration, contact time, adsorbent dose, initial concentration of adsorbate and adsorbent, and particle size. The results showed that the kinetics of adsorption and extent of adsorption at equilibrium depended on physical and chemical characteristics of adsorbent. The adsorption reactions correlate with Langmuir, Freundlich, Bhatacharya, Venkobachar model. The efficiencies of adsorbent materials for the removal of Cr(VI) and Ni(II) were found to be between 56.2 and 96.2% and 83.6 and 100% , respectively. The removal efficiency for Cr^{6+} is Activated Carbon > Bagasse > Fly Ash. For Ni^{2+}, is Activated Carbon > Fly Ash > Bagasse.

2.3.8 Bagasse Fly Ash as Adsorbent for Removal of Other Substances

Not only was bagasse fly ash used to remove heavy metals, but to remove organic and inorganic water pollutant as well. **Gupta and Ali (2001)** investigated to removal of **DDD** [2,2-Bis(4-chlorophenyl)-1,1-dichloroethanel] and **DDE** [2,2-Bis(4-chlorophenyl)-1,1-dichloroehenel] pesticides from wastewater using bagasse fly ash, a sugar industry waste. They found that the DDD and DDE were removed up to 93% at pH 7.0, with the adsorbent dose of 5 g/L of particle size 200-250 μm at 30°C and shaking time of 80 min. The removal of these two pesticides was achieved up to 97-98% in column experiments at a flow rate of 0.5 mL/min. The adsorption was found to be exothermic in nature, takes place by particle diffusion mechanism and follows both Langmuir and Freundlich models.

Gupta et al. (2002) studied removal of **lindane** and **malathion** from wastewater using bagasse fly ash–a sugar industry waste. They found that the optimum contact needed to reach equilibrium was found to be 60 min. Maximum removal takes place at pH 6.0 the removal of the pesticides increases with an increase in adsorbent dose and decreases with adsorbent particle size. The optimum adsorbent dose is 5 g/L of particle size 200-250 μm. The material exhibited good adsorption capacity and followed both Langmuir and Freundlich models. At lower concentrations, adsorptions was controlled by film diffusion, while at higher concentrations, it was controlled by particle diffusion mechanisms.

2.3.9 Low-Cost Materials as Adsorbent for Heavy Metals Removal

However, some research studied other inexpensive absorbent. For example, **Gupta (1998)** studied equilibrium uptake, sorption dynamics, process development, and column operations for the removal of Copper and Nickel form aqueous solution and wastewater using activated slag, a low-cost adsorbent. The results showed that the waste material can be fruitfully employed for the removal of these metals in a wide range of concentrations.

Namasivayam and Senthilkumar (1998) investigated to removal of Arsenic (V) from aqueous solution using industrial solid waste that focus on adsorption rates and equilibrium studies. **Gupta and Sharma (2002)** studied the removal of Cadmium and Zinc from aqueous solutions using red mud which is an aluminum industry wastes. **Naseem and Tahir (2001)** studied removal of Pb(II) using bentonite as an adsorbent. **Bereket and others (1997)** studied removal of Pb(II) ,Cd(II), Cu(II), and Zn(II) by adsorption onto bentonite. **Yu and others (2001)** investigated the removal of lead and copper by sawdust.

2.3.10 Adsorption and then Cement Fixation

This research is aim to treatment metal by bagasse and bagasse fly ash and cement fixation, some researches focus on fly ash. **Weng and Huang (1994)** studied treatment of metal industrial wastewater by **fly ash** and cement fixation. The results showed that the fly ash has been demonstrated to be a potential heavy metal adsorbent for **Zn(II)** and **Cd(II)** in dilute industrial wastewaters. Fly ash adsorption capacities for Zn(II) and Cd(II) were 0.27 and 0.05 mg/g, respectively. Although fly ash has low metal adsorption capacity compared to that of activated carbon, it can be obtained cheaply in large quantities and used as a neutralizing agent in the treatment process. The compressive strength of the mortars decreased with increasing content of fly ash or metal-laden fly ash. However, by replacing the cement with up to 10% metal-laden fly ash, the strength of mortar cured for 56 days is about the same as or even greater than that of the reference samples. The results indicated that, for an extended curing time, it was possible to prepare mortars with metal-laden fly ash that have strength as high as that with cement only. Leachate from the fixed metal-laden fly ash, obtained using both the ASTM and USEPA-EP, exhibited metal concentrations lower than the drinking water standards. The fixation process can be environmentally safe. Compressive strength and leaching test results suggest that metal-laden fly ash can be considered for use in secondary construction materials.

2.4 Theory of Cr(VI) Reduction

2.4.1 Concepts and Definitions

Chemical reduction is a process in which the oxidation state of a substance is reduced. Conversely, chemical oxidation is a process in which the oxidation state is increased. For simple inorganic oxidation-reduction (redox) reaction, oxidation is equivalent to a loss of electrons, and reduction to a gain of electrons. This definition is not directly applicable to organic reactions. The purpose of oxidation/reduction in water and wastewater treatment is one of converting undesirable chemical species to species which are neither harmful nor otherwise objectionable (Weber, 1972).

Any material which functions as an electron acceptor is an oxidizing agent and a reducing agent is any material which serves as an electron donor. In this reasoning, a given element can assume the role of either an oxidizing agent or reducing agent, depending upon its oxidation state and on reaction conditions. For example, equation 6), iron(II) is a reducing agent when reacting with manganese dioxide,

$$2Fe^{2+} + MnO_2 + 2H_2O + 2OH^- \longrightarrow Mn^{2+} + 2Fe(OH)_3 \qquad 2.6)$$

where as iron(III) oxidizes hydrogen sulfide to elemental sulfur as shown in equation 7):

$$2Fe^{3+} + H_2S \longrightarrow 2Fe^{2+} + S^0 + 2H^+ \qquad 2.7)$$

Since no oxidation reaction occurs without a concomitant reduction reaction, the overall process is referred to as an oxidation-reduction (redox) reaction.

The concept of electron exchange is still very useful, particularly for inorganic reaction, as it affords a quick and simple means for balancing redox reactions. With regard to a mechanistic interpretation of oxidation processes, however, there are two drawbacks associated with the electron transfer concept 1) it dose not represent the actual state of affairs (i.e., many redox reactions, for which a very simple overall equation can be written, do not proceed via a direct transfer of electrons) and 2) with respect to organic oxidations (involving covalent bonds), the concept is not directly applicable because it is difficult to distinguish between different oxidation states (Weber, 1972).

2.4.2 Role of pH in Chemical Oxidations

Oxidation rates may be affected by pH as a result of one or a combination of the following effects (Weber, 1972):

1. Changes in free energy of the overall reaction
2. Changes in the reactivity of reactants
3. Specific OH^- ion or H_3O^+ ion catalysis

pH is one of the most influential parameters in oxidation reactions, and that it should be carefully monitored and/or controlled in chemical oxidation process.

2.4.3 Nature of Reactants

Effectiveness is often increased by adjusting pH and by addition of catalysts to the reaction system. The free-energy change, activation energy, and the actual reaction mechanism naturally depend on the nature of both the oxidizing and the reducing agent. In fact several independent mechanisms may be operative simultaneously for two given reactants (Weber, 1972).

2.4.4 Cr(VI) Reduction by Chemical Processes

Ronald et al. (1997) investigated to reduction of Cr(VI) by amorphous iron sulfide, they found that amorphous iron sulfide minerals like mackinawite (FeS_{1-x}) have the potential to reduce large quantities of Cr(VI) and in the process form very stable [Cr, Fe] $(OH)_3$ solids and it can reduced between 85% and 100%. **Bond et al. (2003)** studied kinetics and structural constraints of chromate reduction by green rusts (ferrous-ferric iron oxides). The results indicated that the rates of reduction are controlled by the concentration of ferrous iron, surface area, and chemical structure of the green rust including layer spacing. Green rust chloride is the most rapid reductant of Cr(VI) followed by $GRCO_3$ and $GRSO_4$, with pseudo-first-order rate coefficients ranging from 1.22×10^{-3} to 3.7×10^{-2} s^{-1}. **Williams and Scherer (2001)** studied kinetics of Cr(VI) reduction b carbonate green rust. The results show that the rate of Cr(VI) reduction was proportional to the green rust surface area concentration, and pseudo-first-order rate coefficients ranging from 1.2×10^{-3} to 11.2×10^{-3} s^{-1} were determined. The effect of pH was small with a 5-fold decrease in rate with increasing pH (from 5.0 to 9.0). **Griend (2002)** investigated for kinetics and mechanism of chromate reduction with hydrogen peroxide in base. The results indicated that the reaction is first order in Cr(VI) and inhibited by hydroxide. Hydrogen peroxide anion initially attacks chromate, and subsequent equilibrium steps that exchange oxo group for three peroxo groups precede a rate-determining, one-electron, intramolecular reduction step. **Maxcy et al. (1998)** studied a kinetic of reduction of Cr(VI) to Cr(III) by thiourea. They found that reproducible kinetic data were obtained for the reduction of Cr(VI) by thiourea in the pH range of 4.0 to 5.0 and the reaction rate increases with increasing concentrations of Cr(VI), thiourea, hydrogen ion, and acetate buffer.

2.4.5 Cr(VI) Reduction by Biological Processes

In addition to chemical methods, the potential for biological treatment of Cr (VI) has been demonstrated. Many microorganisms of genera can reduce Cr(VI) such as, **Wang and Shen (1997)** studied modeling Cr(VI) reduction by pure bacterial cultures. They found that each Cr(VI)-reducing species may possess a finite Cr(VI) reduction capacity, which is not influenced by subsequent cell growth during Cr(VI) reduction. **Konovalova et al. (2003)** investigated to Cr(VI) reduction in a membrane bioreactor with immobilized *Pseudomonas* cells. The results show that reduction is suppressed by high metabolite concentrations, which reaced on the sixth step of chromate adding in studied system. **Guha et al. (2001)** studied kinetics of Cr(VI) reduction by a type strain *Shewanella alga* under different growth conditions, their studied show that, successful *in situ* bioremediation of Cr(VI) is depended on the type of substrates (electron donors. **Chirwa and Wang (2000)** investigated to simultaneous Cr(VI) reduction and phenol degradation in an anaerobic consortium of bacteria. This study illustrates that phenol can be used as the sole added carbon source for Cr(VI) reduction in an anaerobic consortium. However, the system relied on the availability of organic acid intermediates during anaerobic phenol degradation.

2.4.6 Low-Cost Materials as Reductant

Many low-cost materials were examined for the treatment of chromate-containing solution, as an alternative and more economical reducing agent for Cr(VI) such as **Reddad et al. (2003)** studied mechanism of Cr(III) and Cr(VI) removal by using sugar beet pulp. They found that the reduction mechanism for Cr(VI) was achieved at acidic pH values. The carboxylic groups of the sugar beet pulp were found to be the main reduction sites of Cr(VI) species. **Erdem et al. (2004)** studied reduction of Cr(VI) by siderite. The results show that, the Cr(VI) reduction efficiency of the siderite was found to be strongly depended on acid content of the solution. The maximum Cr(VI) reduction yield for 50 mg/L initial concentration is obtained in the presence of 20 g/L siderite for 120 min. The reduction capacity of siderite was calculated as about 17 mg-Cr(VI)/g siderite. **Gardea-Torresdey et al. (2000)** investigated to characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural by products of *Avena nonida* (Oat) biomass. The results suggest that binding of Cr(VI) and subsequent reduction of Cr(VI) to Cr(III) is somehow catalyzed by the oat biomass. **Park et al. (2004)** studied reduction of Cr(VI) with the brown seaweed *Ecklonia* biomass. They found that the Cr(VI) remoal efficiency was always 100% in the pH 1-5. The rate of Cr(VI) reduction increased with decreasing the pH and the electrons required for the Cr(VI) reduction also caused the oxidation of the organic compounds in the biomass. One gram of the biomass could reduce 4.49 0.12 mmol of Cr(VI). **Zouboulis et al. (1995)** studied removal of Cr(VI) anions from solutions by pyrite fines (an industrial by-product). They found that the Cr(III) ions generated by the Cr(VI)/pyrite interfacial reduction process are subsequently hydrolysed. The interfacial reduction of chromium was found to proceed faster in the acidic pH range (around 1-2). **Stasinakis et al. (2004)** studied investigation of Cr(VI) reduction in continuous-flow activated sludge systems, they found that, reduction of Cr(VI) by activated sludge was independent of the acclimatization of biomass to Cr (VI) and it was enhanced by an increase of retention time and organic substrate acts as an electron donor for Cr(VI) reduction.

2.4.7 Adsorption and Reduction of Cr(VI)

Aggrawal et al. (1999) investigated to adsorption of chromium by activated carbon form aqueous solution. They found that the quinonic groups in activated carbon can cause reduction of Cr(VI) into Cr(III) ions. In case of oxidixed carbons two processes are occurring simultsly: the increase in the removal of Cr(VI) due to its reduction to Cr(III) by theacidic quinonic groups and the decrease in adsorption of Cr(VI) ions due to thation of acidic surface groups. The optimum pH for the reduction of Cr(VI) to) ions is around five. **Cimino et al. (2000)** studied removal of toxic cations anVI) from aqueous solution by hazelnut shell. The results showed that hazelnut shows also effective capacities of Cr(VI) removal. This process works only the limits of a short acid pH interval (2.5-3.5) where the reduction reactions(VI) and the sorption processes of Cr(III), $HCrO_4^-$ and CrO_4^{2-} ion species are rized. The maximum sorption capacity at pH 2.0 is 17.7 g/kg. **Daneshvar et al.**) studied chromium adsorption and Cr(VI) reduction to trivalent chromium in as solutions by soya cake. This study showed that soya cake can assist in chromiution control, two ways. In the first process, the reductive functional groups in ske structure cause the conversion of Cr(VI) to Cr(III). This reaction has high effr at pH < 1. In the second process, using the adsorptive property of soya cake, am is removed from solution. This process was more efficient in acidic solutioecially at pH = 1 or lower. **Lakatos et al. (2002)** studied coals as sorbents e removal and reduction of hexavalent chromium from aqueous waste strehis investigation has demonstrated that the reduction of Cr(VI) is governed by centration and the extent of electron donor functionalities in the coals. Lowerexhibit larger redox potentials for the Cr (III)/Cr(VI) system, and give rise toredox capacities of the coals. The extent of Cr(VI) uptake by coals achieved in estigation (10-30 mg/g) compares will with those obtained for alternative naturarring materials.

2.5 Portland Cement

Portland cement is the name given to a cement obtained by intimately mixing together calcareous and argillaceous, or other silica-, alumina-, and iron oxide-bearing materials, burning them at clinkering temperature, and grinding the resulting clinker (Neville and Brooks, 1994)

2.5.1 Constituents of Portland cement

At the higher burning temperatures used in Portland cement production, approximately 1450 °C, all the SiO_2-containing components (clays, quartz, etc.) react to achieve, very nearly, an equilibrium phase assemblage. Four compounds are regarded as the major constituents of cement: they are listed in Table 2.2 together with their abbreviated symbols. From this table, it will be noted that the quantities do not add up to 100%, the missing percentages being accounted for by impurities. Each oxide formula is abbreviated to a single capital letter, with the number of oxide formulas in the compound designated by a subscript placed after the letter. The shortened notation, namely: $CaO = C$; $SiO_2 = S$; $Al_2O_3 = A$; and $Fe_2O_3 = F$. Likewise, H_2O in hydrated cement is denoted by H (Taylor, 1992; Neville and brooks, 1994; Neville, 2003; and Mindess, Young and Darwin, 2003).

The batching and calcinations should ensure that silica is chemically combined as C_3S and C_2S, while free CaO is reduced to near zero. The resulting product, which partially melts and sinters during calcinations, is known as clinker. The well-indurated clinker is mixed with 2-5% gypsum and ground to fine powder having a specific surface of 3000-4000 cm^2/g.

The silicate, C_3S and C_2S, are the most important compounds, which are responsible for the strength of hydrated cement paste. In reality, the silicates in cement are not pure compounds, but contain minor oxides in solid solution. These oxides have significant effects on the atomic arrangements, crystal form, and hydraulic properties of the silicates (Figure 2.5).

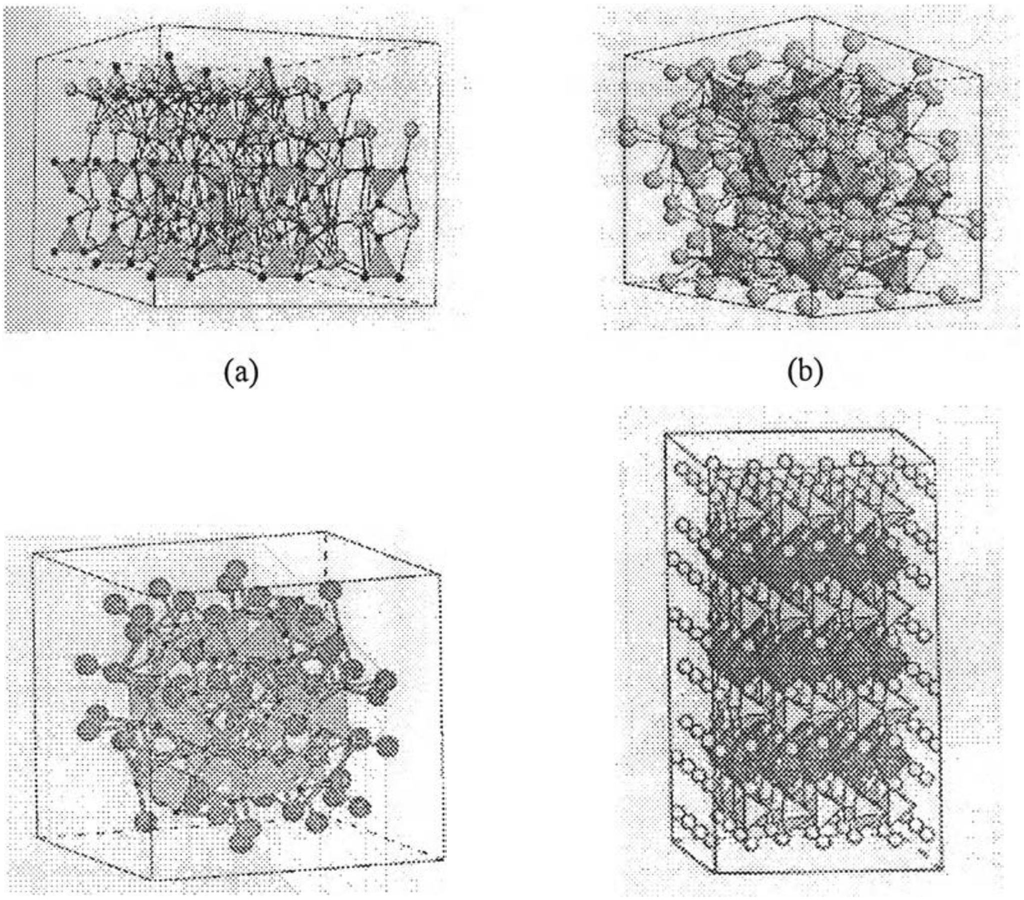
Table 2.2 Main Compounds in Ordinary Portland Cement (Mindess, Young and Darwin, 2003)

Name of compound	Oxide composition	Abbreviation	Weight percent
Tricalcium silicate	$3CaO \cdot SiO_2$	C_3S	55
Dicalcium silicate	$2CaO \cdot SiO_2$	C_2S	18
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	C_3A	10
Tetracalcium aluminoferrite	$4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	8
Calcium sulfate dehydrate (gypsum)	$CaSO_4 \cdot 2H_2O$	CSH_2	6

The presence of C_3A (Figure 2.5) in cement is undesirable because it contributes little of nothing to the strength of cement except at early ages. And when hardened cement paste is attacked by sulphates, the formation of calcium sulphoaluminate (ettringite) may cause disruption. However, C_3A is beneficial in the manufacture of cement in that it facilitates the combination of lime and silica.

C_4AF (Figure 2.5) is also present in cement in small quantities when compared with the other three compounds. It does not affect the behavious significantly, however, it reacts with gypsum to form calcium sulphoferrite and its presence may accelerate the hydration of the silicates.

In addition to the main compounds listed in Table 2.2, there exist minor compounds, such as MgO, TiO_2, Mn_2O_3, K_2O and Na_2O. A general idea of the composition of cement can be obtained from Table 2.3, which gives the oxide composition limits of Portland cements (Taylor, 1992; Neville and brooks, 1994; Neville, 2003; and Mindess, Young and Darwin, 2003).



(a) (b)

(c) (d)

Figure 2.5 Structure Models of Clinker Major Components (a) C_3S, (b) C_2S, (c) C_3A, (d) C_4AF (Bensted and Barnes, 2002)

Table 2.3 Approximate Composition Limits of Portland Cement (Neville and Brooks, 1994)

Oxide	Content (percent)
CaO	60-67
SiO_2	17-25
Al_2O_3	3-8
Fe_2O_3	0.5-6.0
MgO	0.1-4.0
Alkalis (Na_2O and K_2O)	0.2-1.3
SO_3	1-3

2.5.2 Hydration of cement

The term 'hydration' denotes the totality of the changes that occur when anhydrous cement, or one of its constituent phases, is mixed with water. When Portland cement is mixed with water, its constituent compounds undergo a series of chemical reactions that are responsible for the eventual hardening of concrete. Reactions with water are designated hydration, and the new solids formed on hydration are collectively referred to as hydration products. In the presence of water, the silicates and aluminates of Portland cement form products of hydration of hydrates, which in time produce a firm and hard mass-the hardened cement paste. As stated earlier, the two calcium silicates (C_3S and C_2S) are the main cementitious compounds in cement, the former hydrating much more rapidly than the latter. The product of hydration of C_3S is the microcrystalline hydrate $C_3S_2H_3$ with some lime separating out as crystalline $Ca(OH)_2$. C_2S behaves similarly but clearly contains less time (Taylor, 1992; Spence, 1992; Neville and Brooks, 1994; Mindess, et al., 2003). The $C_3S_2H_3$ are described as C-S-H, the approximate hydration reactions being written as shown in equation 2.8), 2.9), and 2.10):

For C_3S:

$$\underset{[100]}{2C_3S} + \underset{[24]}{6H} \longrightarrow \underset{[75]}{C_3S_2H_3} + \underset{[49]}{3Ca(OH)_2} \qquad 2.8)$$

For C_2S:

$$\underset{[100]}{2C_2S} + \underset{[21]}{4H} \longrightarrow \underset{[99]}{C_3S_2H_3} + \underset{[22]}{Ca(OH)_2} \qquad 2.9)$$

For C_3A:

$$\underset{[100]}{C_3A} + \underset{[40]}{6H} \longrightarrow \underset{[140]}{C_3AH_6} \qquad 2.10)$$

The numbers in the square brackets are the corresponding masses, and on this basis both silicates require approximately the same amount of water for hydration. But C_3S produces more than twice as much $Ca(OH)_2$ as is formed by the hydration of C_2S. The amount of C_3A in most cement is comparatively small; its hydrate structure is of a cubic crystalline form which is surrounded by the calcium silicate hydrates. The reaction of pure C_3A with water is very rapid and would lead to a flash set, which is prevented by the addition of gypsum ($CaSO_4$ $2H_2O$) to the cement clinker. The reaction rate of C_3A is quicker than that of the calcium silicates. The bracketed masses of C_3A hydration show that, a higher proportion of water is required than for the hydration of silicates. The hydration characteristics of the cement compounds are summarized in Table 2.4.

Table 2.4 Characteristics of Hydration of the Cement Compounds (Mindess, et al., 2003)

Compounds	**Reaction rate**	**Amount of heat liberated**	**Contribution to cement**	
			Strength	**Heat liberation**
C_3S	moderate	moderate	high	high
C_2S	slow	low	low (initially), high (later)	low
$C_3A + CSH_2$	fast	very high	low	very high
$C_4AF + CSH_2$	moderate	moderate	low	moderate

The general nature of Portland cement hydration appears to involve both dissolution-precipitation reactions as well as direct attack of water on grains of anhydrous cement. Through-solution mechanisms, in which anhydrous solid cement components dissolve, supersaturate the aqueous phase, and finally reprecipitate, mainly as hydrates, are probably of greatest importance during the initial set and hardening: solution-precipitation is very effective in transporting material and gelling the aqueous phase (Spence, 1992). Figure 2.6 summarizes some of the processes involved in early hydration.

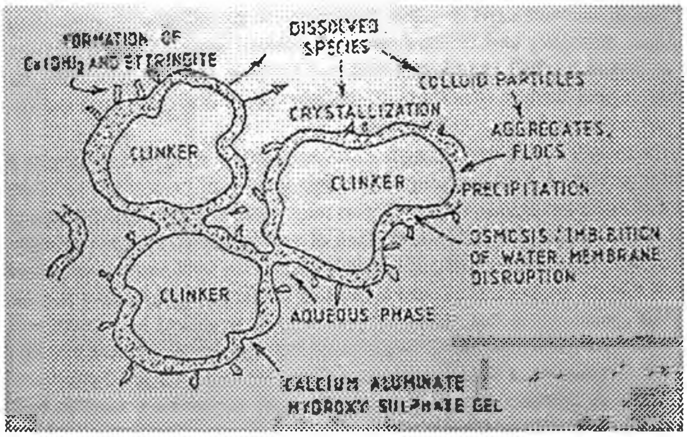


Figure 2.6 Schematic View of Hydration Processes Occurring During the First Few Hours of Days (Spence, 1992)

2.5.3 Pozzolanic Reaction

This reaction is the second step continuing from the hydration reaction. In this step, calcium hydroxide ($Ca(OH)_2$) developed form the hydration reaction, reacts with silica (SiO_2) and alumina (Al_2O_3) from pozzolana material. The chemical equation (Taylor, 1990) as shown in equation 2.11) and 2.12):

$$3\ Ca(OH)_2 + 2\ SiO_2 \longrightarrow 2CaO\ 2SiO_2\ 3H_2O \qquad 2.11)$$

$$3\ Ca(OH)_2 + 2\ Al_2O_3 \longrightarrow 2CaO\ 2Al_2O_3\ 3H_2O \qquad 2.12)$$

Calcium silicate hydrate ($2CaO\ 2SiO_2\ 3H_2O$) and calcium aluminate hydrate ($2CaO\ 2Al_2O_3\ 3H_2O$) strengthen the bond strength of concrete itself. These substances increase bonds between particles of cement paste increasing the strength of concrete.

2.5.4 Strength of concrete

Strength usually gives an overall picture of the quality of concrete because it is directly related to the structure of cement paste. Factors affecting strength as follow:

2.5.4.1 Water-to-Cement Ratio and Porosity

Concrete that is not properly compacted will contain large voids, which contribute to its porosity. Thus, at lower water-to-cement ratios, full compaction is difficult to achieve. Porosity is a primary factor influencing the strength of concrete; it depends upon the water-to-cement ratio and on the degree of hydration. The paste consists of hydrates of the various cement compounds and of $Ca(OH)_2$, and the gross volume available for all these products of hydration consists of the sum of the absolute volume of the dry cement and of the volume of the mix water. In consequence of hydration, the mix water takes one of three forms namely; combined water, gel water and capillary water. Figure 2.7 show the diagrammatic representation of the volumetric proportions of hydration.

The gel water is the water that is held physically or is adsorbed on the large surface area of the hydrates in cement gel. It has been established that the volume of gel water is 28% of the volume of cement gel. The combined water is water which is combined chemically or physically with the products of hydration by very firmly. The solid products of hydration occupy a volume which is less than the sum of the absolute volume of the original dry cement and of the combined water. Then, there is a residual space within the gross volume of the paste. For fully hydrated cement, with no excess water above that required for hydration, this residual space represents about 18.5% of the original volume of dry cement. The residual space takes the form of voids or capillary pores, which can be empty of full of water, depending on the quantity of original mix water and whether additional water. Capillary pores are much larger than gel pores. If the mix contained more water than necessary for full hydration, there will be present capillary pores in excess of the 18.5%.

It is worth noting that while the water-to-cement ratio, a measure of total porosity, is the principal controller of the strength of the cement paste constituent of concrete for given mixing and curing conditions, there are indications that the details of the porosity, as represented by the void size distribution, can have a significant effect on concrete strength. Reduction in the water-to-cement ratio and the addition of silica fume not only results in a reduction in the total porosity, but also reduces the size of the maximum measurable voids within the hardened cement paste.

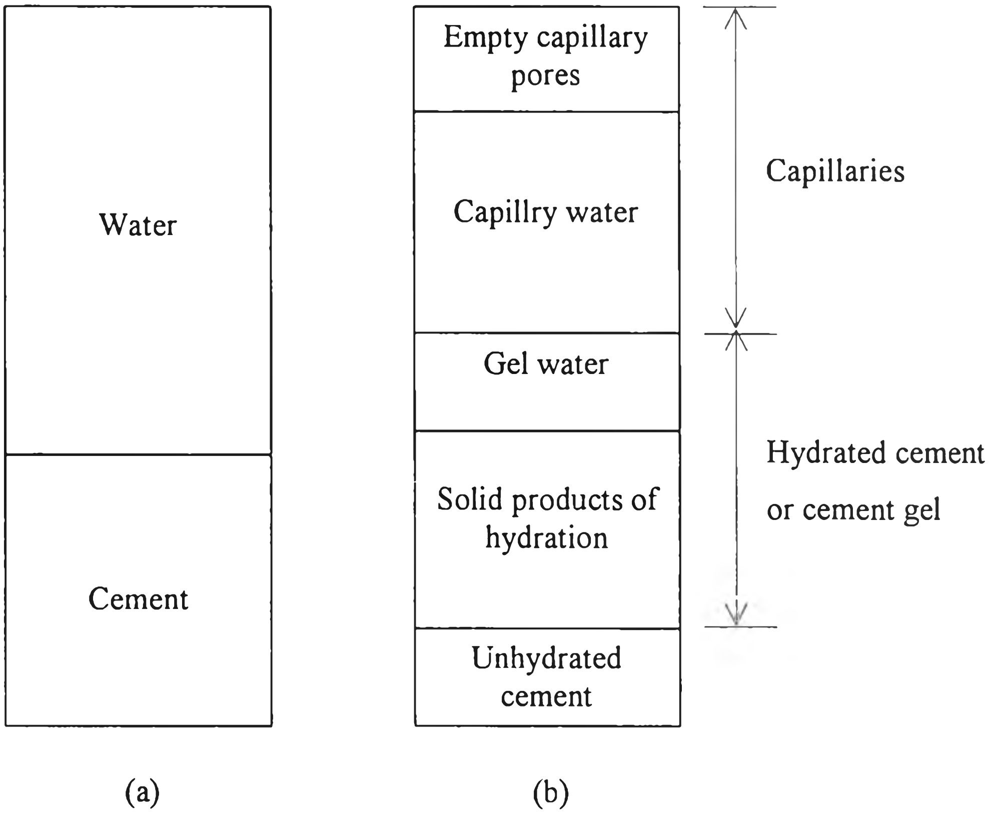


Figure 2.7 Diagrammatic Representation of the Volumetric Proportions: (a) Before Hydration and (b) During Hydration. (Neville and Brooks, 1994)

Although capillary pores are much larger than gel pores, in fact, there is a whole range of pore sizes throughout the hardened cement paste. When only partly hydrated, the paste contains an interconnected system of capillary pores. The effect of this is a lower strength. These problems are avoided if the degree of hydration is sufficiently high for the capillary pore system to become segmented through partial blocking by newly developed cement gel. In this case, the capillary pores are interconnected only by the much smaller gel pores, which are impermeable (Neville and Brooks, 1994; Mindess, et al., 2003).

2.5.4.2 Age

In practice, it is common to obtain 7-day as well as 28-day compressive strengths. Therefore, it would be very useful to extrapolate 28-day strengths from 7-day (or other) strengths. Of course, this depends upon the cement types and curing temperature. As a general rule, the ratio of 28-day to 7-day strength lies between 1.3 and 1.7, but is usually less than 1.5. Generally, the higher the rate of early strength gain over the first three days, the higher the ratio of 7-day to 28-day strength. Once some experience has been gained for particular mixes, the ratio of strengths may prove to be useful on a particular construction project (Mindess, et al., 2003).

2.5.4.3 Cement

The effect of Portland cement on concrete strength depends on the chemical composition and fineness of the cement. The strength of hardened cement paste comes primarily form C_3S (earlier strength) and C_2S (later strength), and these effects carry through into concrete. Concretes made with higher C_3S contents gain strength more rapidly, but may end up with slightly lower strengths at later ages (Mindess, et al., 2003). Cement rich in tricalcium silicate showed high strength at early ages, while those which were low in this compound showed much lower strength at early ages, but a progressive increase with age, so that at 6 months the differences in the strengths were relatively small. At 12 months the strengths of the two groups of cements were about equal (Mindess, et al., 2003; and Hewlett, 2004).

The effects of cement fineness on the strength of concrete are also considerable, since the rate of hydration increases with increasing fineness and leads to a higher rater of strength gain. However, even though more finely ground cements gain strength more rapidly, very fine grinding should be avoided. With very fine particles, excessive agglomeration may lead to local regions of high water-to-cement ratio.

2.5.4.4 Mineral admixtures

The use of mineral admixtures results in a modification of the structure of hardened cement paste and may result in changes within the interfacial transition zone. For normal-strength concretes, mineral admixtures such as fly ash and blast furnace slag can be used to replace Portland cement, with little effect on strength. The other major pozzolan, silica fume, is generally used to increase strength and will do so even at the same water-to-cement ratio. The combined pozzolanic and filler effects of silica fume also increase the strength and greatly decrease the porosity of the interfacial transition zone compared to that obtained in concretes without the admixture (Mindess, et al., 2003).

2.5.4.5 Chemical admixtures

Chemical admixtures per se have very little effect on the strength of concrete, except insofar as they affect the water-to-cement ratio or the porosity of concrete. For instance, air-entraining agents principally affect concrete strength due to the increase in porosity. Even in this case, however, the reduction in water content obtainable through the use of entrained air may actually results in an increase in strength for concretes with low cement contents designed for a constant workability (Mindess, et al., 2003).

2.5.4.6 Aggregate

The nature of the bond between cement paste and aggregate in concrete has been proposed that, the bond is composed of both chemical interactions and mechanical interlocking, possibly provided by epitaxial growth of certain cement hydrates onto the surfaces of the aggregate particles. For normal-strength concretes, the aggregate parameters that are most important are the shape, texture, and maximum size of the aggregate. The aggregate texture depends on whether the aggregates are naturally occurring gravels, which tend to be smooth, or crushed rocks, which tend to be rough and angular. Surface texture affects both the bond and the stress at which microcracking begins, but has little effect on the compressive strength of the concrete. At low water-to-cement ratio, crushed rock will lead to higher concrete strengths because of the better mechanical bond, but this effect disappears as the water-to-cement ratio increases.

The use of a larger maximum size of aggregate affects the strength in several ways. Under compressive load, the larger aggregate particles tend to cause a greater stress concentration and a resulting reduction in compressive strength. In the range of aggregate contents normally encountered, the exact volume of aggregate is only of secondary importance in determining concrete strength. If a constant workability is maintained, however, the strength of concrete is principally dependent on the cement content, because of the reduced water requirement as the aggregate size is increased (Mindess, et al., 2003; Hewlett, 2004).

2.5.4.7 Minor components

Cement strength may be affected by the presence of minor constituents in clinker, may be present only in amounts of a few percent, or a few tenths of a percent. The effect of MgO content on cement strength has been studied by several investigators and has been found not to be very significant. Free lime affected the strength mainly by inducing unsoundness, volume instability and cracking (Hewlett, 2004).

2.5.5 Cement Replacement

In addition to utilization as binders in S/S process for heavy metals, various types of waste materials can be used as cement replacement materials. For example, **Elinwa and Mahmood (2002)** used **sawdust ash** from timber waste as cement replacement material. The result showed that 10% replacement of cement with sawdust ash showed good performance giving the desired workability and strength.

Kula et al. (2002) investigated on the use of **tincal ore waste**, **fly ash**, and **coal bottom ash** as portland cement replacement materials. The results showed that compressive strength of all specimens containing 1 wt.% of tincal ore waste was higher than that of the control at the 28th day of curing. At 90 days, the contribution to strength by bottom ash + tincal ore wastes and fly ash + tincal ore wastes was higher than in the concrete prepared equivalent tincal ore waste beyond 3 wt.% of Portland cement replacement. Adding bottom ash or fly ash with tincal ore waste improved the performance relative to tincal ore waste replacement only. Increasing replacement of tincla ore waste gives rise to a higher setting time. As a result, tincal ore waste, bottom ash and fly ash samples may be used as cementitious materials.

Rachakornkij (2000) studied the utilization of **municipal solid waste incinerator (MSWI) fly ash** in cement mortars. The results showed that both two type of MSWI fly ash: chemically treated and untreated, significantly enhanced compressive strengths of mortar specimens. XRD analyses showed the formation of a new phase, $C_3A.CaCl_2.10H_2O$ (Hydrocalumite), which was detected only in the fly ash paste. High adsorption capacity of the fly ashes and the formation of hydrocalumite helped to improve the compressive strengths.

2.5.6 Blended cements or lime-pozzolan binders

Blended cements or lime-pozzolan binders recently have become an interesting alternative for social construction in developing countries. Scientists are always in search of waste materials which can be used as a blending component in cement to improve its quality and reduce the cost. Some researches focus on bagasse ash, for example: **Singh, Singh, and Rai (2000: 1485-1488)** studied hydration of **bagasse ash**-blended Portland cement. They found that in presence of bagasse ash setting times increased and free lime decreased. The compressive strength values, in the presence of 10% bagasse ash, were higher than those of control at all ages of hydration and increased with hydration time. The blended cement was found to be more resistant in an aggressive environment. The results indicate that bagasse ash acts as a pozzolanic material.

Hernandez and others (1998) investigated to use of wastes from the sugar industry as pozzolan in lime-pozzolan binders. The wastes under investigation were **sugarcane bagasse ash** (SCBA) and **sugarcane straw ash** (SCSA). The SCBA was extracted directly from the boilers of the sugar factory in Cuba. SCSA was sampled from the heaps of open-air burnt straw in Mexico and Cuba. The results of the study showed that sugarcane bagasse ash can be classified as a probable pozzolanic material. However, high temperatures and incomplete combustion that take place in the boilers influenced its reactivity, which in some cases could be negligible. The main factors that affect the reactivity are the degree of crystallinity of the silica present in the ash and the presence of impurities, such as carbon and unburned material. The sugarcane straw ash showed good pozzolanic activity comparable to that of rice husk ash.

2.6 Solidification/Stabilization (S/S) process

2.6.1 Definition of S/S process

The term “solidification/stabilization’ (S/S) refers to a category of waste treatment processes that are being used increasingly to treat a wide variety of wastes-both and liquid (Spence, 1992; Means, et al., 1995). Generally, S/S processes are designed and used to accomplish one or more of the following objectives:

- Reduce contaminant/pollutant mobility or solubility
- Improve the handling and physical characteristics of the waste by producing a solid with no free liquid
- Decrease the exposed surface area across which transfer or loss of contaminants may occur.

Stabilization refers to techniques that chemically reduce the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization.

Solidification refers to techniques that encapsulate the waste, forming a solid material, and does not necessarily involve a chemical interaction between the contaminants and the solidifying additives. The product of solidification, often known as the waste form, may be a monolithic block, a clay-like material, a granular particulate, or some other physical form commonly considered "solid."

Figure 2.8 illustrates the chemical/structural challenge and the several types of interactions that may occur in the solidified system. A waste chemical component may chemisorb, precipitate, form a surface compound to any of several cement component surfaces, form inclusions or be chemically incorporated into the cement structures, or have simultaneous occurrence of several of these situations (Spence, 1992).

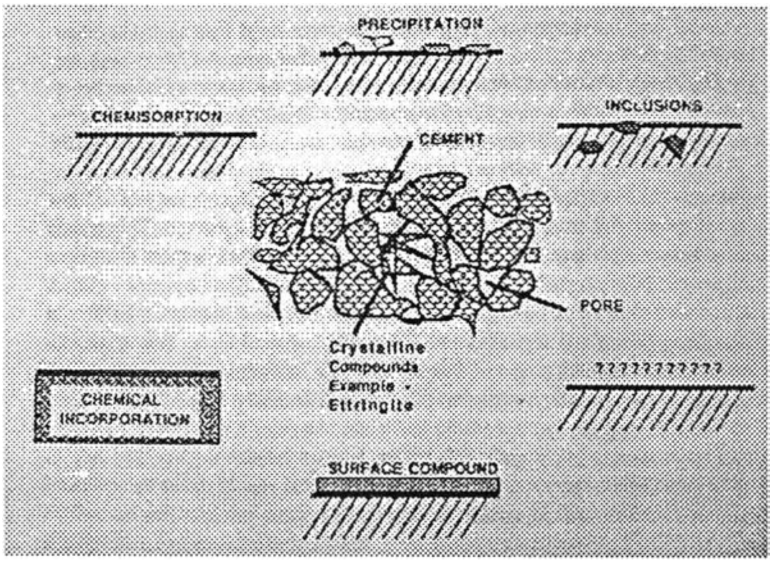


Figure 2.8 Various Possibilities for the Interaction of Hazardous Substances with Cement (Spence, 1992)

2.6.2 Type of S/S process

Generally, S/S processes can be grouped into inorganic processes (cement and pozzolanic) and organic processes (thermoplastic and thermosetting polymers) as shown in Figure 2.9. In addition to the individual use of inorganic and organic binders, some systems combine organic with inorganic binders (Spence, 1992; U.S. EPA., 1989; and Means, et al., 1995).

2.6.2.1 Inorganic S/S

Inorganic binders: the two principal types of inorganic binders are cement binders and pozzolanic binders. A pozzolan is a material containing silica or silica and alumina that has little or no cementation value itself, but under some condition, can react with lime to produce cementitious material; for example, lime, kiln dust, and fly ash. This probably is attributable to the low cost of the materials or waste, their applicability to a wide variety of waste types, and the ease of operation in the filed.

2.6.2.1.1 Cement-based S/S

Cement-based S/S is a process in which waste materials are mixed with Portland cement. Water is added to the mixture, if it is not already present in the waste material, to ensure the proper hydration reactions necessary for bonking the cement. The wastes are incorporated into the cement matrix and, in some cases, undergo physical-chemical changes that further reduce their mobility in the waste-cement matrix. Typically, hydroxides of metals are formed, which are much less soluble than other ionic species of the metals. Small amounts of fly ash, sodium silicate, bentonite, or proprietary additives are often added to the cement of enhance processing. The final product may vary form a granular, soil-like material to a cohesive solid, depending on the amount of reagent added and the types and amounts of wastes S/S.

To improve immobilization of specific contaminants, S/S process may be used in conjunction with sorbents or other additives. Additives can decrease the mobility of contaminants in the pores and can also be incorporated to mitigate the effects of certain inhibitors. For example, additives, soluble silicates, clays, emulsifiers and surfactants, certain sorbents (e.g., carbon, silicates, zeolitic materials, and cellulosic sorbents), activated carbon, lime (CaO or $Ca(OH)_2$), soda ash (Na_2CO_3), fly ash, sodium hydroxide (NaOH), organophilic calys, organosilanes.

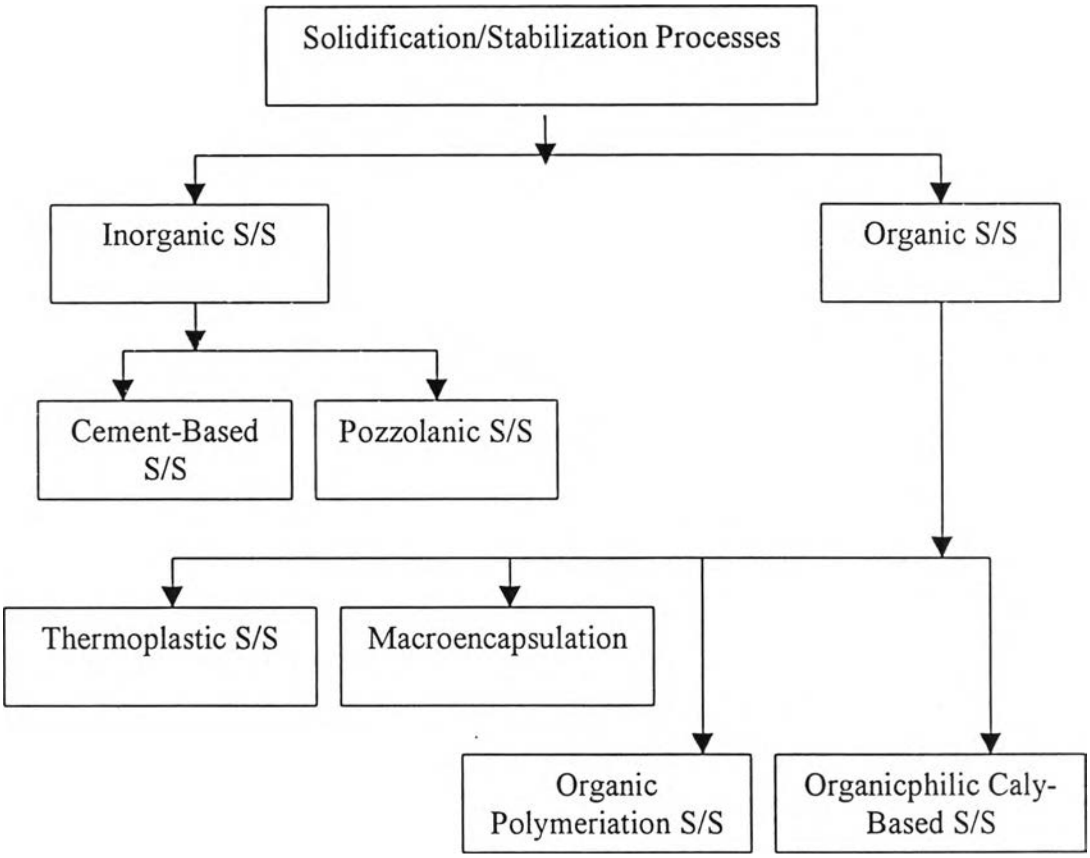


Figure 2.9 Type of Solidification/Stabilization Process (adapted from U.S. EPA., 1989).

2.6.2.1.2 Pozzolanic S/S

Pozzolanic S/S involves siliceous and aluminosilicate materials, which do not display cementing action alone, but form cementitious substances when combined with lime of cement and water at ambient temperatures. The primary containment mechanism is the physical entrapment of the contaminant in the pozzolan matrix. Examples of common Pozzolanic are fly ash, pumice, lime kiln dusts, and blast furnace slag. Pozzolans contain significant amounts of silicates, which distinguish them from the lime-based materials. The final product can vary from a soft fine-grained material to a hard cohesive material similar in appearance to cement. Pozzolanic reactions are generally much slower than cement reactions.

2.6.2.2 Organic S/S

Organic binders: organic binders that have been tested or used for S/S include the followings: asphalt (bitumen), polyethylene, polyesters, polybutadiene, epoxide, urea formaldehyde, acrylamide gel, and polyolefin encapsulations. The basic types of organic S/S processes are thermoplastic and thermosetting.

2.6.2.2.1 Thermoplastic S/S

Thermoplastic S/S is a microencapsulation process in which the waste materials do not react chemically with the encapsulating material. In this technology, a thermoplastic material, such as asphalt (bitument) or polyethylent, is used to bind the waste constituents into a S/S mass.

2.6.2.2.2 Macroencapsulation

Macroencapsulation is a process that places the waste in an overpack drum. The waste is generally S/S and (sometime) microencapsulated prior to drumming. The Environmental Protection Polymers process chemically S/S a sludge with lime or cement. This material is them agglomerated by a polybutadiene binder (actually representing microencapsulution). The polybutadiene agglomerated the waste by a thermosetting reaction in a polymertization process at temperatures of 120° to 200°C. After that the waste matrix is encapsulated which accomplished with polyethylene resin.

2.6.2.2.3 Organic polymerization S/S

Organic polymerization S/S relies on polymer formation to immobilize the constituents of concern. Urea formaldehyde is the most commonly used organic polymer for this purpose. This process has been used primarily to S/S radioactive wastes.

2.6.2.2.4 Organophilic clay-based S/S

This technology appears to be very promising in terms of binding organic wastes. Recent investigations indicate that these organophilic binders truly bond with organic wastes, and when forced out, these waste molecules break down into smaller fragments. Further, this process appears to be cost-effective compared with incineration. Because this technology also used cementitious materials, it can handle both organic and inorganic wastes.

2.6.3 Immobilization Mechanisms

Waste stabilization may involve physical mechanisms, chemical mechanisms, or a combination of the two (Spence, 2000; U.S. EPA., 1989; and Means, et al., 1995).

2.6.3.1 Physical mechanisms

Physical mechanisms of S/S operate by confining waste constituents to a certain area or zone in the waste. That is, the waste constituent may or may not occur in a soluble form, but one or more physical barriers prevent its mobilization.

Containment by a barrier is a satisfactory method as long as the barrier remains stable. Encapsulation is the most commonly used method of containment, superseding earlier use of sorbents.

Encapsulation techniques use materials that trap waste constituents in the form of stable solids, preferable as a monolith with high cohesive strength and low leachability. The effectiveness of isolates waste constituents from groundwater and air depends on the permeability and long-term stability of the matrix and on the degree of mixing of waste constituents throughout the matrix. Encapsulation of inorganic wastes is generally accompanied by chemical stabilization, but for organic wastes usually occurs without accompanying chemical interaction. It can be described at three levels: microencapsulation, macroencapsulation, and embedment.

2.6.3.1.1 Microencapsulation

The term microencapsulation describes a process of adsorbing or trapping contaminants in the pore spaces of a cementitious material. The contaminants are fine waste particles that may not be visible to the naked eye. As the system ages, the waste and matrix may eventually become a homogeneous material, although this might occur in a time frame of thousands of years or more.

2.6.3.1.2 Macroencapsulation

The term macroencapsulation describes a process of coating a solid or cemented waste with an impermeable layer, such as bitumen or amorphous silica. The success of this method depends on both effective coating reactions and thorough mixing.

2.6.3.1.1 Embedment

The term embedment described a process of incorporating large waste masses into a solid matrix before disposal. It is used in situations where it is impractical to reduce the bulk of the waste but where the waste is hazardous enough to be treated prior to disposal. In addition, special consideration may also have to be given to the strength, water permeability, and long-term stability properties of the matrix.

2.6.3.2 Chemical mechanisms of inorganic wastes

2.6.3.2.1 Basic chemical equilibria

The chemistry of inorganic waste constituents is dominated by hydrolysis reactions. The term hydrolysis implies that a substance, usually a metal, reacts with water. Hydrolyzed products can react in the aqueous phase to form new ionic or neutral species, or they can form precipitates of hydroxides, oxides, or salts.

2.6.3.2.2 Effect of alkaline conditions

Numerous compatible ionic species form solids by coprecipitation. Therefore, the application of chemical equilibira based on pure end-members may not be completely valid. Ferric iron has long been recognized for its ability to flocculate and coprecipitate toxic metals form solution. The minimum solubility of most metal hydroxides occurs within the approximate pH range of 7.5 to 11. This implies that solubility increases under extremely alkaline conditions as well as under acidic conditions. Any alkali may be used to control pH, but the common choices are lime, sodium carbonate, or sodium hydroxide. Most solidification reagents are alkaline and can substitute in part or entirely for traditional alkalies, acting both as pH controls and as binding agents. Alkaline binders include Portland cement, cement and lime kiln dusts, Type C fly ash, and sodium silicate.

2.6.3.2.3 Effect of redox potential

Redox potential is another important solution parameter in S/S technology. Redox reaction is one that involves the transfer of electrons between products and reactants. Among the regulated metals, Cr and Hg have more than one common oxidation state. Trivalent chromium species precipitate as a low-solubility hydroxide. However, Cr(VI) forms mainly chromate and dichromate species which do not form preciptatates with low solubility. While adjustment of the redox-sensitive contaminant to its least soluble oxidation state is an important aspect of chemical stabilization, this objective eventually will be defeated if the treated waste is placed in a disposal or reuse environment having a very different oxidation state. Long-term stability can only be ensured if the oxidation states of the treated waste and the disposal of reuse environment are similar.

2.6.3.2.4 Metal silicates

The behavior of hazardous metals in the silicate system is critical to cement-based S/S technology. Metal silicates are generally nonstoichiometric and poorly crystallied. In fact, their chemical and physical properties depend considerably upon the conditions under which they are formed, for example, temperature, concentration, addition rate, and ionic speciation. The pH is also very important because it affects how readily soluble silicate (or colloidal silica) adsorbs metal ions. It has been found that adsorption occur when the pH is 1 to 2 units below the hydroxide precipitation point. It is believed that C-S-H incorporates metal ions into the silicate matrix during the hydration reaction. The number of metal ions retained decreases as the CaO:SiO_2 ratio in C-S-H increase. If metal have already been precipitated as low-solubility solids, they may gradually react with the silicate (if such a reaction is favorable) as log as frees silicate is available; i.e., before it reacts with other ions in the system, such as calcium. The probable result is that the cementitious matrix will encapsulate the metal solids as hydroxides, sulfides, carbonates, etc. Continued reaction of metal ions with silicate will occur only if a continuous source of soluble silica can be created within the matrix or if the waste is pretreated to dissolve the metal hydroxides.

2.6.3.2.5 Other low-solubility phases

Another alternative to precipitating metals as hydroxides is to bind them using insoluble substrates. Insoluble starch xanthates have been widely used for this purpose since they became commercially available in 1980. Wastes stabilized by xanthates are less sensitive to pH and have better sludge dewatering properties than metal hydroxides.

2.6.3.3 Chemical mechanisms of organic wastes

As with inorganic wastes, organic constituents can undergo reactions including hydrolysis, change of oxidation state, and precipitation as some form of salt. Hydrolysis normally involves the loss of hydroxyl group (-OH) in exchange for another functional group. Reactions must be catalyzed by a strong base to proceed at reasonable rates. Oxidation can be made to occur by treating the waste with strong oxidizing agents such as potassium permanganate.

2.6.4 Physical factors affecting S/S

The following physical characteristics of the waste can affect the setting time, curing time, strength, and other physical and chemical properties of the final waste form: particle size and shape, free water content, solids content, specific gravity/density, viscosity, temperature and humidity (U.S. EPA., 1989; and Means, et al., 1995).

2.6.5 Chemical factors affecting S/S

Many of compounds, materials, and factors are effects to S/S process. The effects are many and varied and are not simple to predict from knowledge of the composition of the waste. Often, a number of species are present, sometimes with opposing effects. The some species may have opposite effects depending on concentration. Some of the general effects are interesting. Ion exchange can inhibit of retard S/S reactions by removing calcium from solution, preventing it from entering into the necessary cementitious reactions. It can also accelerate the process by removing interfering metal ions from solution. Other metals may retard and inhibit the reactions by substituting for calcium in the cementitious matrix (U.S. EPA., 1989; and Means, et al., 1995).

2.6.6 S/S Process of Heavy Metals using Cement

Wang and Vipulanandan (2000) studied solidification/stabilization of **Cr (VI)** with cement leachability and XRD analyses. They investigated specimens with curing time of 28 days and varied Cr(VI) concentration of 0.5%, 2%, and 5% (base on K_2CrO_4) by weight of the cement. The result showed that Cr(VI) retarded the initial and final setting times of cement by interfering with the normal hydration process. The cement hydration process was affected in the presence of Cr(VI) because part of the Ca^{2+} in the cement reacted with CrO_4^{2-}.

2.6.7 S/S Process of Heavy Metals using Cement and Additives

Some researchers used bagasse as a stabilizing agent for heavy metal wastes solidified/stabilized in cement. **Janusa and others (2001)** studied an alternative use for **bagasse**: stabilizing agent for **lead** waste. Lead nitrate was used as waste with a 10 and 15% lead by weight to cement loading. Samples were cured for 7, 14, and 28 days at 24 °C. The result showed that samples containing bagasse typically resulted in TCLP extract lead concentrations of approximately 0.5 mg/L of lead for all samples, while samples containing no bagasse had lead extract concentrations of approximately 5 mg/L for 10% samples and 45 mg/L for 15%. The results indicate that using bagasse as an additive to cement is effectively improving the solidification/stabilization of lead.

There are many researchers who aim to reduce harm of heavy metal by using various materials. For example, **Vempati et al. (1995)** investigated to solidification/stabilization (S/S) of toxic metal wastes using **coke** and **coal** combustion by-products. The study has been conducted to evaluate the NISCO cyclone ash (NCA) for S/S **As** (15 µg/mL), **Ba** (500 µg/mL), **Cr** (15 µg/mL), **Pb** (15 µg/mL), and **Zn** (1000 g/mL). The results show that this alkaline waste can retain low concentrations of toxic metal ions, since Leachate concentrations of the metal investigated were well below regulatory levels.

Palomo and Palacios (2003) studied alkali-activated cementitious materials alternative matrices for the immobilization of hazardous wastes: stabilization of **chromium** and **lead**. They focused on alkali activation of **fly ash** and used chromium 2.6% of Cr(VI) in the form of CrO_3 and lead 3.125% of Pb(II) in form of $Pb(NO_3)_2$. The result showed that the matrix of alkali-activated fly ash was not only unable of solidifying and stabilizing chromium but also can gets null in the presence of 2.6% of such element. Chromium affects the activation mechanism of fly ash and, consequently, its hardening process, since $Na_2CrO_4*4H_2O$ is formed. This compound holds a high solubility. In Portland cement systems, chromium is found in the form of Ca_2CrO_4, which induces a rise in the mechanical strength, compared to samples that do not contain such element. The alkali-activated fly ash was able to solidify and stabilize lead since the analyzed concentrations of this element from leaching were in parts per billion ranges. The mechanism that controls lead leaching in those matrices is diffusion. They found that lead compound formed in the matrix is Pb_3SiO_5 which very insoluble compound. Lead inhibits hydration of Portland cement is such a way that test samples break before they are removed from the moulds.

Filibeli, Buyukkamaci, and Senol (2000) studied solidification of tannery wastes containing high **chromium** concentrations (0.1-0.62 mg/L). The sludge was mixed with cement and additives (**fly ash, sand, square floor waste**) and left to solidify for 28 days. The result showed that, the compressive strengths of all solidified samples were under the Turkish concrete standards. So, these materials can not be used as a construction material but they can be used as a filling material. As the ratio of waste sludge increased, the compressive strength of the resulting solid decreased. The compressive strength of the solidified samples increased, as the proportion of cement and percentage of additives was increased. The increase in the water content in the mixtures caused a decrease in the strengths of the solids and delayed the setting of the cement.

Gervais and Ouki (2002) investigated to performance study of cementitious systems containing **Zeolite** and **silica fume**: effects of four metal nitrates on the setting time, strength and leaching characteristics. The aim of this study is to investigate the effects of **chromium**, **manganese**, **lead** and **zinc** on the mechanical and leaching characteristics of cement-based materials. They used three different matrices made of Portland cement, Portland cement and silica fume, and Portland cement and natural Zeolite. The results showed that setting time was accelerated in presence of chromium, while in presence of manganese, lead and zinc it was delayed. For lead and zinc, a 10% replacement of cement by silica fume and Zeolite, markedly accelerated the setting time compared to the cement-only matrix. Although the early strength development was adversely affected in presence of all four contaminants, the long-term strength was less affected compared to the control materials.

Rha et al. (2000) investigated to stability of **hardened slag** paste for the stabilization/solidification of wastes containing heavy metal ions. They focused on **chromium** ions and **lead** ions. Sodium silicate (Na_2SiO_3) 5% of slag was used as an alkali activator for slag hydration. The physical stability of hardened paste containing partial replacement of slag with fly ash and gypsum was also examined. The result showed that, lead ions retarded the hydration of slag because they formed an insoluble and impermeable thin film. The film around the slag particle interrupted the reaction between water and slag surface. Gypsum induced the structural densification of slag through the formation of Aft and AFm phase. The value of compressive strength increased and lead ion leaching concentration decreased. Chromium ions accelerated the initial hydration of slag and generated aluminate hydrates. The compressive strength increased by gypsum or fly ash and the leaching of chromium ions decreased. Solidification of lead ions was therefore due to the physical encapsulation by the hydrate matrix but solidification of chromium ions was due to the substitution of calcium aluminate hydrates.

2.6.8 Characteristic of S/S Product

Promthong (2003) reported that the characteristic of S/S product according to Notification of Ministry No.6 as follow:

1. Unconfined compressive strength (follow to ASTM D 1633 and D 2166) not less than 3.5 kg/cm^2
2. Density not less than 1.15 ton/m^3
3. Concentration of heavy metal in leachant of extraction fluid meets the standard in leachate extraction procedure.

2.6.9 Leachability

2.6.9.1 Definition

When a waste is exposed to water, a rate of dissolution can be measured. This process call leaching, the water which start call leachant, and contaminated water which has passed through the waste call leachate. The capacity of the waste material to leach is called its leachability (Spence, 2000)

Leaching is a rate phenomenon that hazardous or other undesirable constituents are removed from the waste and into the environment via the leachate. This rate is usually measured and expressed in terms of concentration of the constituent in the leachate. This is because concentration determines the constituent's effects on living organisms, especially humans (U.S.EPA., 1989).

2.6.9.2 Leaching mechanisms

Leaching of a porous medium in the field is generally modeled by solute transport equations that incorporate the following factor (Spence, 2000; and U.S.EPA., 1989):

- Chemical composition of waste and leaching medium.
- Physical and engineering properties (e.g., particle size, porosity, hydraulic conductivity) of the waste and surrounding materials.
- Hydraulic gradient across the waste.
- Accumulation of waste species in the pore solution at the particle surface.
- Concentration of reactive species (e.g., H+, complexing agent) in the pore solution at the particle surface.
- Bulk chemical diffusion of the waste or reactive species within the leachate pore solution or waste form.
- Polarity of the leaching solution and waste species.
- Oxidation/reduction conditions and competing reaction dinetics.

2.6.9.3 Factors affecting leachability

There are two sets of factors which affect the leachability of a treated waste: (1) those which originate with the material itself and (2) those which are a function of the leaching test or the disposal environment. The combination of the two sets determines the leachability of the material. They include surface area of the waste, the nature of the extraction vessel, the agitation technique, the nature of the leachant, the ratio of leachant to waste, the number of elution used, the time of contact, temperature, pH of the leachant, and the method used to separate extract from solid (Spence, 2000).

2.7 Concrete Blocks

2.7.1 Interlocking Concrete Paving Blocks

Interlocking Concrete Paving Blocks means solid units of concrete that can be laid together to interlock and form laying patterns. The blocks may be left in their natural color and pigments may be added in the composition; they may receive pigments only on the waving layer. The blocks shall be manufactured in any shape as suitable for movement construction such as roads, foot paths, parking lots and storage floors depending on the design of surfacing and basecourse in accordance with the duty they perform (TIS 827-2531)

The use of small stone elements to create a hard surface for roads or pavements is an ancient tradition that can be traced back to the royal processional roads of ancient Babylon, continuing in Greek and Roman times. Concrete block paving continues this tradition and was first introduced in Holland after the Second World War followed by other countries (notably Germany) and its introduction to the UK in the 1970s. Concrete block paving is a unique material, exhibiting important differences to other small element paving such as stone and clay, as well as to formless materials such as asphalt and insitu concrete. It provides a hard surface which is good to look at, comfortable to walk on, extremely durable and easy to maintain. It adds a richness, complexity and human scale to any setting.

Blocks are fully engineered products manufactured in the factory to give consistency and accuracy. The resulting interlocking characteristics of concrete block paving give it a distinct advantage over other forms of surface. Laid on a granular laying course and with an edge restraint, individual blocks interlock with each other to act together, distributing large point loads evenly. Concrete block paving can be used immediately after the laying procedures have been completed and requires only minimal maintenance.

Concrete block paving is available in a constantly expanding variety of shapes, sizes, colours and finishes and can be installed in numerous bonds and laying patterns, enabling it to delineate space or focus on specific features. Colours are formed from UV stable pigments which are an integral part of the block mix. Some blocks are multi-colour or brindle, formed from batches of two or more colours - such as black, red and buff - which are then blended together. Concrete block paving, often with an irregular or 'weathered' appearance, can match the look of stone setts, cobbles, clay bricks and other traditional surfaces while costing significantly less and providing better slip resistance and a more accessible surface for all pedestrians.

2.7.2Concrete Wall Block

Concrete Wall Block was separated into 2 types namely: hollow concrete block and solid concrete block. The hollow concrete block involved load-bearing block and non-load-bearing block. In this research was studied hollow non-load-bearing concrete as shown in Figure 2.10. Hollow non-load-bearing concrete block is meaning to a walling unit which made from Portland cement, water, and suitable aggregates with or without the inclusion of other materials and with one or more large holes or cavities passing through the block. Its net cross sectional area in every plane parallel to the bearing surface is not less than 75% of its gross cross sectional area measured in the same plane (TIS 58-2530).

2.7.3 Dimensions and tolerances

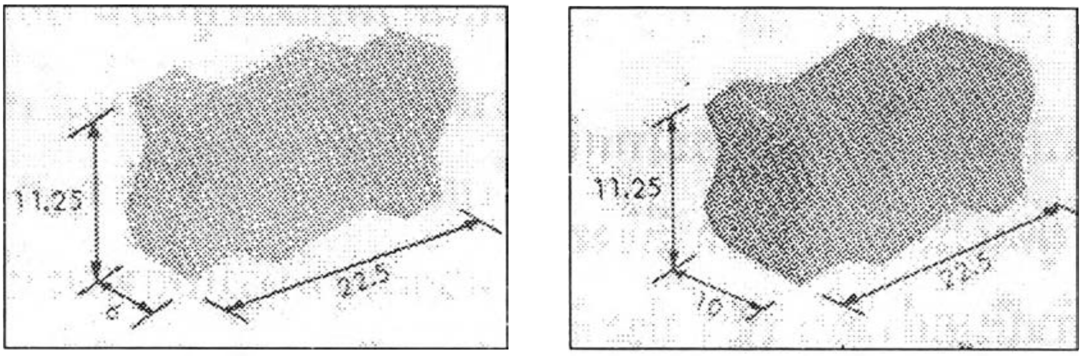
According to TIS 827-2531, lists the requirement of interlocking concrete paving blocks, as shown in Table 2.5. Hollow non-load-bearing concrete block, according to TIS 58-2533, lists the requirement as shown in Table 2.6. In the research, examples of interlocking concrete paving blocks and hollow non-load-bearing concrete block were shown in Figure 2.10 and 2.11, respectively.

Table 2.5 Dimensions and Tolerances of Interlocking Concrete Paving Blocks (TIS 827-2531)

Dimensions	Requirement (millimeter)	Tolerances (millimeter)
Width	< 295	± 2
Length	< 295	± 2
Thickness	60 , 80	± 2
	100, 120	± 3
Thickness of wearing layer (For colored wearing surface only)	3 at minimum	

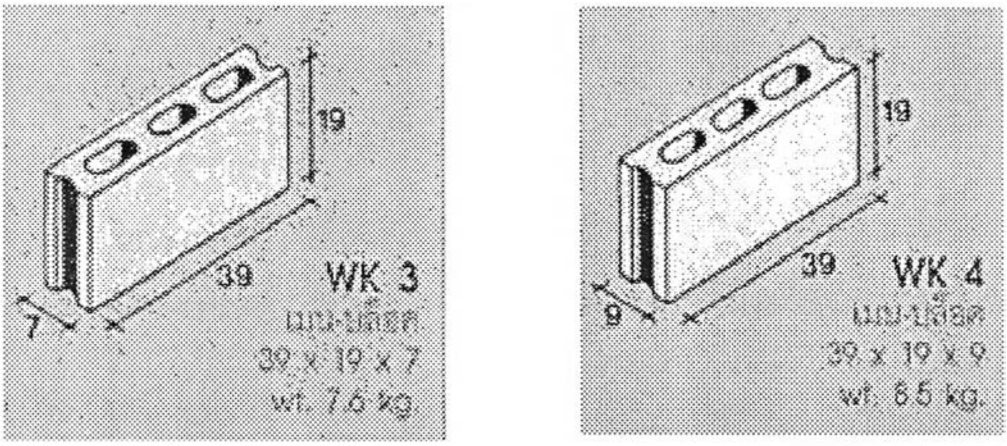
Table 2.6 Dimensions and Tolerances of Hollow Non-Load-Beating Concrete Blocks (TIS 58-2530)

Dimensions	Requirement (millimeter)	Tolerances (millimeter)
Width	70 , 90	± 2
Length	390	± 2
Thickness	190	± 2
Thickness of face-shell	12 at minimum	



(a) (b)

Figure 2.10 Interlocking Concrete Paving Blocks (a) Thickness 60 mm. and (b) Thickness 100 mm (TIS 827-2531).



(a) (b)

Figure 2.11 Hollow Non-Load-Beating Concrete Blocks (a) Width 70 mm. and (b) Width 90 mm (TIS 58-2530).

2.7.4 Compressive Strength

According to TIS 827-2531 and TIS 58-2530, list the requirement of compressive strength of interlocking concrete paving blocks and hollow non-load-bearing concrete block, respectively as shown in Table 2.7.

Table 2.7 Requirement of Compressive Strength of Concrete Block (TIS 827-2531 and TIS 58-2530)

Type of block	Minimum compressive strength (MPa)	
	Individual block	Average block
Interlocking concrete paving blocks	35	40
Hollow non-load-bearing concrete blocks	2.0	2.5

2.7.5 Use recycled aggregates in concrete block

Poon et al. (2002) developed a technique for producing concrete bricks and paving blocks using recycled aggregates obtained from construction and demolition waste. They found that the replacement of coarse and fine natural aggregates by recycled aggregates at the levels of 25 and 50% had little effect on the compressive strength of the brick and block specimens, but higher levels of replacement reduced the compressive strength. Using recycled aggregates as the replacement of natural aggregates at the level of up to 100%, concrete paving blocks with a 28-day compressive strength of not less than 49 MPa can be produced without the incorporation of fly ash, while paving blocks for footway uses with a lower compressive strength of 30 MPa and masonry bricks can be produced with the incorporation of fly ash.