CHAPTER 2

LITERATURE REVIEW

2.1 WASTE TREATMENT TECHNOLOGIES

The waste that remains after the implementation of waste minimization must be treated to detoxify and neutralize them. The treatments can be classified into biological, thermal, physico-chemical and stabilization and solidification methods (Holmes *et al.*, 1993).

2.1.1 Biological Methods

Biological treatment can be classified in many ways. Based on flow configuration, a system can be batch or continuous flow with or without recycling of biomass. Biological treatment is the degradation of organic waste by the action of microorganism. Biological treatment of almost any organic hazardous waste can be accomplished because virtually all organic chemicals can be degraded if the proper microbial communities are established, maintained and controlled. The advantage of this treatment is rapid decontamination of containment and the disadvantage is capital costs can be high and the process may require soil dewatering.

2.1.1.1 Conventional Method

The typical hazardous wastes treated by this method include contaminated ground water and industrial process wastewater containing toxic organic substances. This method consists of passing aqueous hazardous waste through a reactor containing either suspended or attached biomass of highly active and acclimated microorganisms. Flow can be continuous or batch and the reactor can be operated under aerobic or anaerobic conditions. Oxygen is added in aerobic systems by diffused or surface aeration.

2.1.1.2 In-Situ Bioremediation

In situ bioremediation is the method of treating contaminated ground water and subsurface contaminants where they are found without excavating the overlying soil. It is practiced in the aerobic mode with anaerobic processes holding future promise for special applications. It is accomplished by introducing nutrients and oxygen or other electron acceptors to the contaminated site so that microbes can actively degrade the contaminants in the place. The success of the method depends on microbiological, hydrological, geochemical and engineering factors. Bioremediation is attractive because it is a natural process generating harmless residues such as carbon dioxide and water. A major advantage of bioremediation over other hazardous waste disposal is that the biological approach degrades the target chemical and not merely transfers the contaminants from one medium to the other.

2.1.2 Solid-Phase Treatment

The term solid-phase treatment represents a broad class of biological methods which feature treatment of sludge, solids and contaminated soils at conditions of no or minimal free moisture. There are three categories of solid-phase treatment namely, land treatment, composting and heaping. Removal of organics can occur by various mechanisms other than biodegradation. Primary examples are volatilization and leaching. Nevertheless, for any method to qualify as 'treatment', reduction in organics due to biological degradation should dominate abiotic losses and immobilized amounts.

2.1.3 Physico-Chemical Process

The physico-chemical processes include technologies that can be used for hazardous waste treatment and recycling, as well as for ground water or soil remediation.

2.1.3.1 Air Stripping

Air stripping is a mass transfer process that enhance the volatilization of compounds from water by passing air through water to improve the transfer between the air and water phases. It is one of the most commonly used process for remediating ground water contaminated with volatile organic compounds (VOCs) such as solvents. The process is ideally suited for low concentration (<200 mg/L). Air stripping can be performed by using packed towers, tray towers, spray systems, diffused aeration or mechanical aeration. Packed towers are generally used for the specific application of remediation of ground water.

2.1.3.2 Soil Vapor Extraction (SVE)

Soil Vapor Extraction is a relatively new remedial option utilized to remove volatile organic compounds (VOCs) from soils in the vadose zone (the unsaturated zone above the ground water table) or from the stockpiled, excavated soil. The SVE process consists of passing an air stream through the soil, thereby transferring the contaminants from the soil matrix to the air stream. Modifications of the process are distinguished by the location of the treatment system and the method for developing airflow. SVE systems are implemented by installing vapor extraction wells or perforated piping in the zone of contamination and applying a vacuum to induce the movement of the soil gases.

2.1.3.3 Carbon Adsorption

Adsorption is a process in which a soluble contaminant (the adsorbate) is removed from water by contact with a solid surface (the adsorbent). The adsorbent most widely used in environmental applications is carbon that has been processed to significantly increase the internal surface area (activated carbon). Use of different raw materials and processing techniques results in a range of carbon types with different adsorption characteristics. Activated carbon is available in both powdered and granular form.

Granular activated carbon (GAC) is most commonly used for removal of a wide range of toxic organic compounds from ground water and industrial waste streams.

2.1.4 Thermal Method

Incineration systems are designed to destroy only organic components of waste. However, most hazardous waste is non-exclusive in its content and therefore will contain both combustible organics and non-combustible inorganics. By destroying the organic fraction and converting it to carbon dioxide and water vapor, incineration reduces the waste volume and to extent that the organic components include toxic components, its threat to the environment. Incineration is a rather simple chemical process when viewed superficially. Organic compounds are confined to those containing carbon, hydrogen and sometimes oxygen, with the possible addition of metals and non-metals such as halogens and nitrogen.

2.1.5 Stabilization and Solidification (S/S)

Stabilization and Solidification have been widely applied in the management of hazardous wastes. The technologies are being applied to the remediation of hazardous waste sites, the treatment of residue from other treatment processes (e.g., the ash from thermal treatment) and the treatment of contaminated land where large quantities of soil containing contaminants are encountered. In general, stabilization is a process where additives are mixed with waste to minimize the rate of contaminant migration from the waste and to reduce the toxicity of the waste. Solidification is a process employing additives by which the physical nature of the waste is altered during the process. Thus, objectives of stabilization and solidification would encompass both the reduction in waste toxicity and mobility as well as improvement in the engineering properties of the stabilized material.

2.2 TREATMENT METHODS FOR POME SLUDGE

There are various types of POME treatment; ponding system, open tank digester with extended aeration system and closed anaerobic digester & land application. Figure 2.1 shows schematic flow diagram for ponding system. In this system the raw sludge first enters a de-oiling tank where oil is removed. Then it is channeled to a series of two acidification ponds. The acidification phase of anaerobic digestion thus occurs in the first two ponds and is separated from the methanogenic phase which takes place in the next two ponds.

The hydraulic retention times (HRT) of the acidification ponds are 2 days while the HRT for primary anaerobic pond and anaerobic maturation ponds are 30 days and 15 days respectively. Sludge from the bottom of the two anaerobic ponds is pumped out to sand beds for dewatering. The dry solids are sold as fertilizer. Part of the supernatant from the second anaerobic pond is mixed at a 1:1 ratio with raw sludge entering the acidification pond. This also provides a cooling as well as buffering and seeding effect on the raw sludge entering the system. The rest of the anaerobic liquor from the second anaerobic pond goes into a series of four facultative ponds with 4 days HRT.

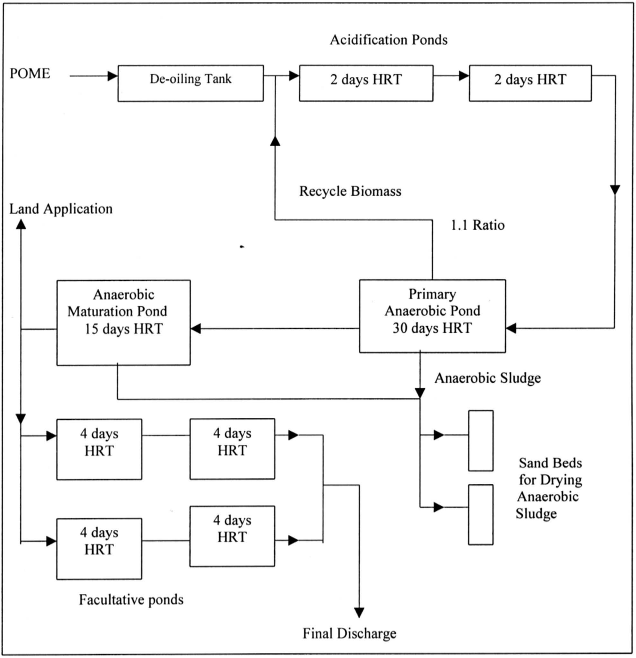

Figure 2.1 Schematic flow diagram for ponding system (Sastry *et al*, 1995)

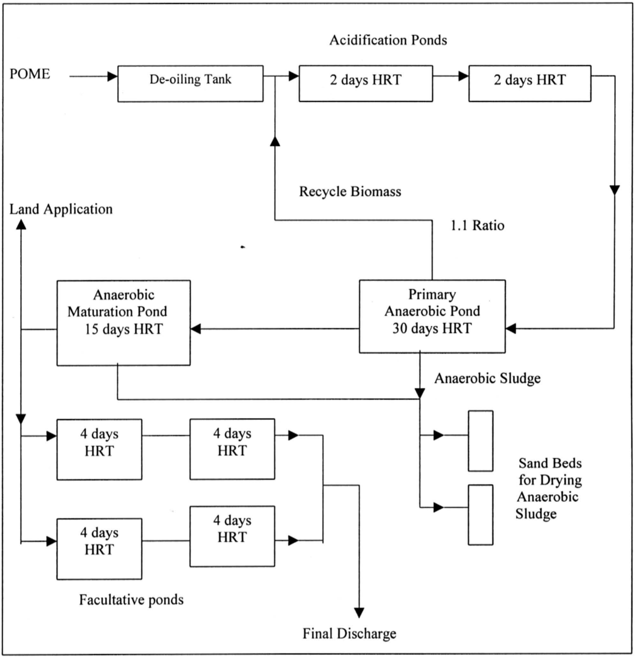

Figure 2.1 Schematic flow diagram for ponding system (Sastry *et al*, 1995)

Another method for POME treatment is open tank digester and extended aeration system (see Figure 2.2). Referring to this figure, the raw sludge is first pumped to acidification pond with 1 day HRT. Then the effluent enters two anaerobic tanks digesters with 20 days HRT and the temperature of the tank contents is kept constant around 45^{0}C. The tank digesters are desludged everyday and the solids being sent to the estate for land application. The anaerobic supernatant from the tank digesters are then sent to a anaerobic settling pond of 1 day HRT which follows by extended aeration pond with the use of mechanical surface aerators for 20 days HRT. From this pond, the supernatant then goes into settling tank for 2 days HRT. From this pond, the liquid is cleaned enough to be discharged for land application.

Figure 2.3 shows a schematic flow diagram of closed anaerobic digester. In this treatment the raw sludge is first pumped from the sludge pit into 2 series of anaerobic digester 1 and 2 for 10 days HRT before it enters the digester effluent sump. The treated effluent is then discharged for land application.

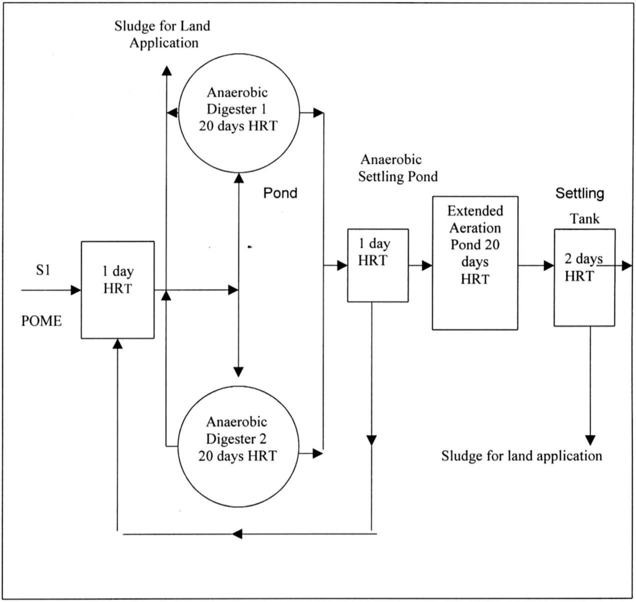

Figure 2.2 Schematic diagram of open tank digester and extended aeration system (Sastry *et al*, 1995)

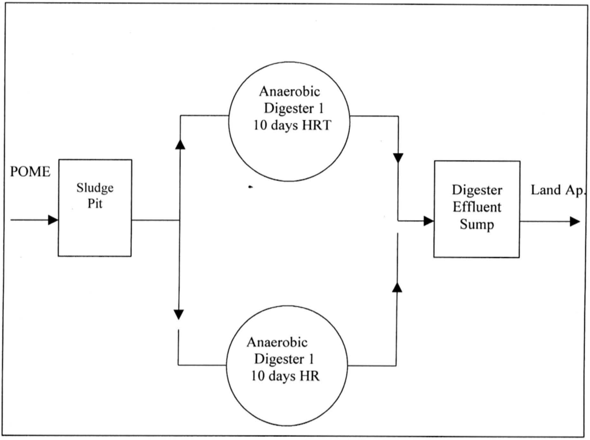

Figure 2.3 Schematic flow diagram of closed anaerobic digester and land application system (Sastry *et al*, 1995)

2.3 COMPARISON OF S/S TECHNIQUE WITH PONDING AND TANK DIGESTER SYSTEMS

Comparison of S/S Technique with ponding and tank digester systems is shown in Table 2.1

Table 2.1 Comparison Between S/S Technique with Present Pome Treatment Methods

NO	PARAMETER	S/S	PONDING	TANK DIGESTER
1	Treatment system	More controlled system since the parameters like W/C, C/S_d, CRM can be controlled	Relatively uncontrolled and exposed system	Controlled system, allowing for mixing and temperature control
2	Cost	Cheap	Expensive	Very expensive
3	Treatment Process	Simple	Complicated	More complicated
4	Premise	Does not require much land	Require large number of ponds, thereby increasing the land area needed	Save land space needed as tanks are deeper than lagoon
5	Mixing	Lack of adequate mixing during the mixing process will result in low compressive strength	Lack of adequate mixing prevents maximum degradation of the wastes and the solid accumulate at such a rate that frequent desludging of the	With complete mixing the solid retention time would be equal to the HRT

			pond is required	
6	Plant Design	Does not require plant design	Through faulty design & operation, a pond may end up as a breeding ground for the flies and be a source of offensive odour	Require proper plants design, operation and management
7	Control & Monitor	Easy	Difficult	Difficult
8	Dewatering Process	Extensive drying or dewatering of waste is not required because cement mixtures require water and the amount of cement added can be adapted through wide ranges of water contents	Not applicable	Not applicable
9	System Tolerance	The system is tolerant of most chemical variations. The natural alkalinity of the cement used can neutralize acids	Not applicable	Not applicable

10	Raw Materials	Relatively large amounts of cement are required but CRM like PFA, CSF, RHA are used to minimize the quantity of cement used	Not applicable	Not applicable
11	Energy	Cement is an energy intensive material	Require high energy to maintain high temperature which outweighs the benefit	Require high energy to maintain high temperature which outweighs the benefit
12	Heavy Rainfall	Little effect as this technique can minimize the leaching of heavy metals from the solidified samples	May cause the pond contents to overflow and pollute surrounding areas like rivers and lakes	Little effect as this system has a cover which prevents the rain from getting in
13	HRT	Not applicable	Longer	Shorter
14	Maintenance	Easy	Difficult to control seapage , oil gets accumulated with solids brought up by the biogas, a sticky oily scum is formed. Require good "house-	Difficult to control seapage , oil gets accumulated with solids brought up by the biogas, a sticky oily scum is formed

			keeping" which mainly entails regular weed and grass trimming and other uses measures to prevent mosquito breeding. Floating scums and mats must be removed	
15	Supervision	Do not require intensive supervision	Require periodic visits by operators to ensure that the pond is operating satisfactorily. When the characteristic green colour of a pond changes to grey or, it is generally a sign of overloading and anaerobic conditions, often accompanied by malodours. When this occur as a result of temporary overload, the wastewater maybe by-passed for some time to allow the pond to restore itself	Extensive operation and management by product personnel

2.4 THE ECONOMICS OF S/S COMPARED TO PONDING AND TANK DIGESTER SYSTEMS

Most waste materials that are currently being considered for disposal have no present value, and thus all S/S costs represent additional expenses to be added to the ultimate cost of the product or service sold. A complete economic analysis must consider costs of waste transportation, materials and equipment required for S/S, skill levels of treatment plant operators, fees or royalties for use of patented processes and cost of transportation and landfilling treated wastes. This type of analysis often must be undertaken on a case-by-case basis. However, to obtain an initial impression of the usefulness of different waste treatment systems now and in the future, it is possible to restrict economic considerations to present and projected costs for materials, equipment and energy.

In most treatment systems, the cost of materials required is the major item regulating present and projected costs. Table 2.2 outlines the present and future economic considerations for major waste S/S systems while Table 2.3 outlines the economic analysis of ponding and tank digester systems.Actually it is very subjective to compare those treatment methods in term of cost since those treatments are definitely different from one another. Compared to those methods, S/S is relatively cheaper. In The United States, S/S treatment is applied by using the batch process in which the sludge is treated in a big truck. The final solidified samples are directly disposed in burial land nearby.

Table 2.2 Present and Projected Economic Considerations for Waste S/S Systems

Type of Treatment System	Major Materials Required	Unit Cost of Material	Amount of Material Required to Treat 100 lbs of raw waste	Cost of Material Required to Treat 100 lbs of Raw Waste	Trends in Price	Equipment Costs	Energy Use
Cement-based	Portland cement	$0.03/lb	100 lb	$3.00	Stable	Low	Low
Pozzolanic	Lime Flyash	$0.03/lb	100 lb	$3.00	Stable	Low	Low
Thermoplastic (Bitumen based)	Bitumen Drums	$0.05/lb $27/drum	100 lb 0.8 drum	$18.60	Bitumen prices are rising rapidly because of oil price	Very Low	High
Organic polymer (polyester system)	Polyester Catalyst Drums	$0.45/lb $1.11/lb $17/drum	43 lb of polyester-catalyst mix	$27.70	Price could rise rapidly due to oil shortage	Very high	High
Surface encapsulation (polyethylene)	Polyethylene	Varies	Varies	$4.50	Price could rise rapidly due to oil shortage	Very high	High
Self-cementing	Gypsum	*	10 lbs	*	Stable	Moderate	Moderate
Glassification/mineral synthesis	Feldspar	$0.03/lb	Varies	-	Stable	High	Very high

- Negligible but energy cost for calcining are appreciable

Table 2.3 Economic Analysis of the Ponding and Tank Digester Systems

Ponding	Tank Digester
1. Land Total land area : 3 ponds = 4.00 ha Fringing land = 1.00 ha Total = 5.00 ha The commercial value of unplanted estate land is estimated at MR$13 000 per ha (but it also depends on the land location) Therefore; Total cost of the land = MR$ 65 000	1. Land Total land area = 1 ha The commercial value of unplanted estate land is estimated at MR$13 000 per ha (but it also depends on the land location) Therefore; Total cost of the land = MR$ 13 000
2. Ponds Excavation cost at MR$ 12 000 per pond = MR$ 36 000 Laying of pipes, pumps, channels, grass turfing of the pond sides = MR$ 35 000 Total capital cost = MR$ 71 000	2. The cost for tank digester of 60 FFB/tones size = MR$1.5 million Therefore; Total capital cost= MR$ 1.513 million

2.5 PREVIOUS STUDIES ON POME UTILIZATION

Studies by various groups have demonstrated such an application was beneficial to oil palm, besides the tremendous saving on fertilizer cost. Several methods of land application of POME to oil palms are currently being practiced (Sharma, 1997). On hilly areas, flatbeds and furrows are employed to ensure uniform effluent distribution to all palms. On flat land with good infiltration, a portable sprinkler system is found to be applicable to mature oil palms. The same system when applied to immature oil palms resulted in frond scorching, while on very clayey and poorly permeable soils, effluent flooding hinders harvesting and loose fruit collection in the fields The use of long beds is being introduced in such conditions. In commercial scale schemes, which are installed at most mills, the logistics, cost and efficiency of various methods are continuously being viewed to ensure maximum benefit (Sharma, 1997).

Various treatments like biological, mechanical, chemical, land disposal and incineration of POME had been studied (Olie and Tjeng, 1972; Muthurajah, 1975; Wood, 1977; Davis, 1978; Foo and Raj, 1978; Diprose and Edwards, 1980; John, 1981; Ma *et al.* 1981; Maheswaran, 1981; Phang, 1982 1987; Yeow, 1983). Utilization of POME as an substrate to grow micro-organisms such as *Neurospora sitophila, Aspergillus niger, Saccharomyces sp, Spirilina platensis, Chlorella sp, Merismopedia, Monoraphidium, Euglena, Trichoderma harzianum, Myceliophthora thermophilia* and *Trichoderma viride* to produce protein-rich biomass which could be harvested as animal feed supplement had been studied by several researchers (Sivalingam, 1980; Phang, 1982; Phang and Ong, 1981, 1988; Vikineswary, 1988; Mohamed Ismail and Ahmad Qalam, 1989). High costs of the fermenters and a poor market discourage this approach to POME treatment (Leelavathy, 1991)

Dunlop Bioprocesses Limited, London and Dunlop Estates Berhad, Malaysia developed another alternative method, Prolima. The process involved the treatment of POME through biological, chemical and physical means insludging biodegradation of the effluent using micro-organisms and their separation to improve the quality of the effluent by reducing the BOD load. After fermentation, the solid fraction was easily removed by filtration to produce a valuable animal feed. The process had been disbanded due to the high cost of production (Kanapathy *et al.* 1983).

Land treatment of municipal, agricultural and industrial wastes could be a cost-effective and efficient means of pollution control and resource recovery (Loehr *et al.* 1979). In the attempts to safely dispose the POME, early workers used land application as a viable alternative. Treating the raw POME merely to reduce its organic load and then discharging it into waterways is wasteful of a valuable resource (Wolman, 1977). Land disposal of POME by way of trench or ridge was suggested by Singh and Hoong (1968). After applying large quantities of liquid POME on the land, Wood (1977) found that at first, vegetation was killed and percolation was blocked leading to anaerobic conditions that led to odour and insect problems. He also reported that if POME was applied to indisturbed soil in relatively small doses at a time, the effluent dried up, leaving a parchment like layer of humus which on drying, cracked and flaked up. Foo and Raj (1978) concurred that land disposal of raw POME is possible provided a small quantity at a time was applied, otherwise, odour and insect pests could pose a problem (Leelavathy, 1991).

2.6 CURRENT STABILIZATION AND SOLIDIFICATION PROCESS

Stabilization and solidification processes are "non-destructive" methods to immobilize the hazardous constituents in a waste. Typically, S/S processes physically sorb, encapsulate or change the physicochemical form of the pollutant in the waste, resulting in a less leachable product. Concentration of contaminants in the treated waste are often lower than in the untreated waste, primarily because of incidental dilution by the binder rather than by destruction or removal of the contaminants. S/S processes can generally be grouped into organic and inorganic processes. Inorganically based stabilization processes are generally more favorably applied to inorganic wastes, especially those containing cations. Organic processes are more suitable for organic anionic wastes (Jeffrey *et al.*, 1995).

2.6.1 Organic Process

Organic encapsulation methods have generally been used in specialized application where cost has not been an overriding factor (e.g. radioactive waste disposal) and are usually too expensive to be considered appropriate for large volumes of industrial waste. Organic processes are almost infinite in potential variety, but for practical purposes would best be limited to systems such as asphalt, tar, polyolefin and epoxies which are inexpensive enough to be, at least in theory, applied to the problem.

Unfortunately, inexpensive is a relative word and the systems, in fact, can become quite expensive when compared to current disposal cost for wastes to which they are applied. There are other problems. These are primarily hydrophobic in nature and difficulties are encountered when incorporating the water-based wastes that make up the primary disposal problem. In addition, organic systems suffer from the problem of instability with regard to ambient environmental factors such as microorganisms and ultraviolet light.

2.6.1.1 Thermoplastic Technique

Thermoplastic materials such as asphalt, bitumen, polyethylene, paraffin and polypropylene are organic plastics capable of reversible softening and hardening on heating and cooling. In this technique, the residue needs to be either dry or dewatered to high solids content and is then mixed with the polymer at an elevated temperature of about 100 ^{0}C. The process can be both continuous and batch mixing and is energy intensive in operation. Sulphur has been incorporated in the encapsulating matrix to improve physical strength and structural integrity.

2.6.1.2 Organic Polymer Techniques

The major organic polymer technique used is the urea-formaldehyde process. A monomer is added to the waste/sludge and mixed before the catalyst is added. The polymerized material does not generally combine chemically with the waste. A spongy mass is formed that traps the solid particles while permitting some liquid to escape. The polymeric mass can be dried before disposal but is often buried without drying in containers.

2.6.1.3 Encapsulation Techniques

Encapsulation technique is any stabilization process in which the waste particles are enclosed in a coating or jacket of relatively inert materials. Both microencapsulation and macroencapsulation have been utilized to stabilize hazardous waste materials. This technology is effective for high concentration of pollutants and high waste loading. A commonly used process utilizes polybutadiene binder to agromerate the inorganic waste (microencapsulation) followed by the application of a thin polyethylene jacket around the sludge mass (macroencapsulation) to yield a monolithic product with high chemical integrity. The solidified waste must fulfilled governmental requirement in terms of final disposal discharge consents.

2.6.2 Inorganic Process

The important non-proprietary systems involved either portland cements, lime-based mortar, lime-pozzolan cements such as lime-fly ash and some mixed inorganic-organic systems. Coating, impregnation or surface hardening can also be used with both inorganic or organic processes as a way of attempting to isolate a solid mass of waste material from the environment. However, this is useful only where the materials have already been solidified into a form-holding mass.

2.6.2.1 Cement-Based Technique

Cement-based-technique is a process in which waste materials are mixed with ordinary portland cement. This technique is specially effective for waste with high level of toxic metals such as metal-bearing wastes, activated sludge, fly ashes, lead containing wastes, metal fines, inorganic sludge from electroplating and many others. Water is added to the mixture to ensure the proper hydration reactions necessary for bonding the cement. The wastes are incorporated into the cement matrix.

Cement-based process utilizes a mixture of portland cement and sludge along with certain other additives such as fly ash to produce a monolithic, rock like mass for disposal. Portland cement is a fused mixture of calcium, silicon, aluminium and iron oxides. The main constituents are usually dicalcium and tricalcium silicates. Wet wastes or sludge are mixed directly with the cement and other additives, to initially form a colloidal calcium-silicate-hydrate gel of indefinite composition and structure. The hardening of cement is brought about by interlacing of thin, densely packed, silicate fibrils growing from the individual cement particles. These interlocking fibrils incorporate the added aggregates and/or waste into a monolithic, rock-like mass.

Materials in the waste such as sulfides, asbestos, latex and solid plastic wastes may increase the strength and stability of the waste concrete. Whereas certain organic and inorganic compounds can retard setting, cause swelling and reduce final strength. All insoluble materials may be present as dust or may coat the larger particles and weaken the bound between the particles and the cement. Soluble salts of manganese, tin, zinc, copper and lead may cause large variation in setting time and significant reduction in physical strength. Salts of zinc, copper and lead are the most detrimental. Products containing large amounts of sulfate (such as flue gas cleaning sludge) not only retard the setting concrete, but by reacting to form calcium sulfoaluminate hydrate, they cause swelling and spalling in the solidified waste-containing concrete.

A number of additives have been developed for use with cement to improve the physical characteristics of the leaching loses from the resulting solidified sludge. Soluble silicate has reportedly been used to bind contaminants in cement solidification processes, but this additive causes an increase in volume to occur during the setting of the cement-waste mixture. The sodium silicate appears to precipitate most interfering ions in a gelatinous mass and so remove their interference and speed setting. The development of a gel is important in the setting of the cement-waste-silicate mixtures.

Excessive mixing after the gel forms seems to cause slower setting and lessen final strength of the product. Polymer impregnation process and surface coatings are being developed to increase the strength and durability of the cement-waste mixture. It also can be used to decrease the permeability of the concrete-waste mixture. The pores of the concrete-waste are filled by soaking in styrene monomer. The soaked material is then to bring about polymerization. This process results in significant increase in the strength and durability of the concrete-waste mixture. Surface coating of concrete-waste composites has been examined extensively.

The major problems encountered have been poor adhesion of the coating onto the waste or lack of strength in the concrete material containing the waste. Surface coating materials that have been investigated include asphalt, asphalt emulsion and vinyl.

Limitations of this technique are; extensive pretreatment, more expensive cement types or additives may be necessary for waste containing large amounts of impurities such as borates and sulfates that affect the setting of curing of the waste-concrete mixture. Cement is also an energy intensive material.

2.6.2.2 Lime-Based Techniques

Lime-based stabilization techniques generally depend on the reaction of lime with siliceous material and water to produce a hardened material or sometime referred to as a pozzolonic material. The two most common additives used which are waste products themselves are fly-ash and cement-kiln dust. The techniques suffer from setting and curing problems and are generally suited for stabilizing inorganic wastes rather than organic wastes. The decomposition of organic material in the sludge mass after curing can result in increased permeability along with some decrease in the final strength of the final strength of the material.

2.7 STABILIZATION AND SOLIDIFICATION MECHANISMS

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, preferably as a monolith with high cohesive strength and low leachability.

Waste constituents are dispersed throughout an organic or inorganic binder matrix that physically isolates them from groundwater and air. The effectiveness of isolation depends on the permeability and long term stability of the matrix and the degree of mixing of waste constituents throughout the matrix. In practice, mixing may be less than ideal, usually in some of the waste material occupying cavities in the matrix. Encapsulation can be divided in three categories, namely macroencapsulation, microencapsulation and embedment (Hills *et al*, 1992).

2.7.1 Macroencapsulation

The term macroencapsulation has been used to describe processes in which a solid or cemented waste form is coated with, or contained in, an impervious layer to limit access of leachant to the waste itself. It is also sometimes used to describe the encapsulation of large waste agromerates in a solidification matrix-gross version of microencapsulation. The degree of protection attained depends completely on the matrix, coating or container. The coating method has not been used in the hazardous waste field, except for the nuclear wastes.

2.7.2 Microencapsulation

Microencapsulation describes a process of adsorbing or trapping contaminants in the pore spaces of a cementitious material. Most S/S wastes are microencapsulated. The sizes of the microencapsulated particle may range from very small occlusions to larger agglomerates visible under low power light microscopy, or even to the naked eye. Individual particles or agglomerates retain their identities even after through mixing with high-energy devices. At the system ages, the waste and matrix may eventually become a homogenous material even at the microscopic scale, but this transformation might only occur on a geologic time scale.

2.7.3 Embedment

Embedment describes a process of incorporating large waste mass into a solid matrix before disposal. Embedment 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, waste permeability and long-term stability properties of the matrix. It is sometimes necessary or desirable to incorporate discrete waste masses of discernible size into a solid matrix before disposal. Examples are contaminated trash and debris from remedial actions; contaminated personal protective equipment from laboratories, from environmental investigations, or at hazardous waste management facilities; medical solid wastes and highly radioactive objects.

2.8 FACTORS AFFECTING STABILIZATION AND SOLIDIFICATION PROCESS

When the S/S technique is employed in certain treatment processes, there are several factors affecting the S/S process which can be divided into physical and chemical factors.

2.8.1 Physical Factors

There are eight physical factors that are discussed below.

2.8.1.1 Particle Size and Distribution

Particle size in the waste and of the hardened binder can play an important role in the performance of treatment processes. Particle content can impact handling and final product characteristics. Small particles can release the alkalinity quicker, reduce diffusion limitation and increase area availability for sorption/desorption. Small particles, because of the large surface to volume ratio, will generally leach more rapidly (on equal weight basis) than large particles. If there is chemical interaction between the waste particles and the S/S reagents, small particles will tend to react faster. This is easily shown, for example in OPC-soluble silicate systems.

It has been demonstrated by some researchers that very fine particulate can coat the surfaces of reagents and inhibit the setting reactions of cements and pozzolans. Particle sizes of the waste can affect the reaction rate of constituents inside the particles with fixation agents in the S/S formulations. This is especially important when the fixation agents have short lives in the S/S environment, or are immediately destroyed when the next process step study takes place.

Physical properties of the S/S product are affected not only by the particle size but also by the size distribution. Particle size distribution affects a number of waste properties, especially viscosity. Reactivity with the S/S system, wettability, inhibitory effects in some systems and leachability of the final waste form are all influenced in one way or another by this factor. A wide range of sizes generally contributes to a stronger product, as evidenced by the use of a well-graded aggregated distribution in concrete. Particle size distribution also affects pumpability and mixability of wastes.

2.8.1.2 Particle Morphology

Particle morphology or shape is also important especially in the flow of pumable wastes and in the mixing of wastes with a reagent in S/S systems. The effect of spherical particles, such as those from power plant fly ash in reducing viscosity and increasing pumpability of concrete mixes is well known. Typically, spherical particles produce slurries that are fluid up about 50 % solids, while platelet-shaped particle slurries are non-fluid at about 10 % solids. Mixing coarse sand into a viscous slurry, for example $Mg(OH)_2$, actually reduces the viscosity, even though the solids content rises. Acicular particles and fibrous wastes may produce non-pumable mixtures at even lower solids content; for example, some paper industry wastes are virtual solids at about 1 % by weight total solids.

2.8.1.3 Flash Point

Flash point determination is a standard test for liquids. No standard method is available for solids but a useful quick test is to operate a spark generator close to the surface. If the waste is a flammable hazard, it will ignite.

2.8.1.4 Free Water Content

Only free water is available for setting reactions. Some bound water may become available during long-term curing. Water may be immobilized in hydrating particle surfaces.

2.8.1.5 Solids Content

Depending on solid concentration, solids may settle out resulting in two-phase systems or final products may have undesirable strength characteristics. A low solids, low viscosity, high specific gravity waste requires either a fast setting S/S process or the addition of bulking agents. It is virtually impossible to make strong, durable forms with an inorganic S/S system at low solids content.

2.8.1.6 Specific Gravity

If there is a significant difference in the densities of the various phases in a waste, especially between the suspended solid particulate and the medium, phase separation and layering will occur. This may be so rapid as to make homogenization difficult and cause excretion of fluid from the waste form as it cures. Most S/S reagents have specific gravity greater than 2.0 versus 1.0 to 1.5 for typical wastes. Phase separation may take place until setting begins. Rheological agents can also be added to alter viscosity. These agents may subsequently interfere with setting reactions.

2.8.1.7 Viscosity

Viscosity of mixes can change with particle size, shape and specific gravity. It affects the handling of wastes and mixing them with reagents, to the degree that the choice of the mechanical systems is often determined by waste viscosity alone. Generally, as particulate is added to a water medium, viscosity increases gradually and nearly proportionately up to a certain point, after which the viscosity increases very rapidly with small increase in density. Besides, as the average particle size decreases, viscosity increases. Basically, viscosity is a rheological property. It can be defined, as the force required to move a unit area of plane surface with unit speed relative to another parallel plane surface, both surfaces separated by a unit thickness of fluid. It is also defined and measured as the ratio of shear stress to shear rate. Viscosity may also impact phase separation as well as the kinetic of S/S processes.

2.8.1.8 Temperature and Humidity

Typically, rates of reaction increase with temperature. However, temperature below 0 ^{0}C will cause retardation of set while those over 30 ^{0}C will accelerate setting. Temperature over 66 ^{0}C may completely destroy the reactions. Below freezing, gel structures can be broken; at high temperature, steam release can break up solid mass and reduce available water reactions. Some reagents such as kiln dust and fly ash, contain CaO, which can hydrate violently, releasing heat. Ambient curing humidity should be kept high. Evaporation of water from the surface may inhibit solidification.

2.8.2 Chemical Factors

There are four chemical factors that are discussed below.

2.8.2.1 Alkalinity and Acidity

Most inorganic S/S processes can handle a wide pH range, but the extremes can cause problems. Very high pH (>12) is not counteracted and most reagents quickly neutralize very low pH if the total acidity is not too high. It is advisable to partially neutralize the waste to pH 5 or greater with lime or other alkali before solidification. In the case of high pH, it may be important whether the pH comes from small amounts of strong alkali such as NaOH, or from large quantities of lime. Actually, the most important parameter is not pH, but total alkalinity or acidity. The former can have an inhibitory effect; the latter is primarily of concern in the economics of the overall process. The anion associated with the acid may affect setting, for example, in the case of chloride from HCl, but again the quantity is important. Small amounts will usually have no effect on inorganic systems.

2.8.2.2 Composition and Speciation

Soluble species in the waste have considerable effect on setting, causing inhibition or even preventing setting entirely. These species can also act as accelerators. These effects are not always negative, sometimes it is desirable to speed up or slow down normal setting reactions for practical reasons in the process design. For example, delayed setting may be necessary to prevent an excessive viscosity increase in the mixing or conveying equipment.

2.8.2.3 Zeta Potential

The electrochemical surface properties of very small particles, especially in the colloidal state, may have a pronounced effect on viscosity of wastes. This typically occurs in the size range of five microns and smaller. Zeta potential is a measurable quantity that correlates with these effects, and is widely used in wastewater treatment for flocculation tests to determine the type and amount of polyelectrolyte to use. The properties of colloids do appear to influence setting behaviour with some wastes and with some S/S processes, but this area has not been studied sufficiently to establish general cause-effect relationship.

2.8.2.4 Redox Potential

The oxidation state of the system may affect solidification reactions in some cases, although there is no mention in the literature of direct effects. Indirect effects can occur by mechanism such as biological growth as determined by aerobic/anaerobic conditions. Under extreme conditions of oxidation or reduction, organic S/S processes can be substantially affected and some inorganic and organic constituents in inorganic systems may be altered.

2.9 ADVANTAGES AND DISADVANTAGES OF STABILIZATION AND SOLIDIFICATION

Advantages and disadvantages of S/S will vary with the binders, types of waste, process, the site conditions and other unique factors. The advantages of S/S are it can immobilize certain compound, can utilize process by-products such as rice husk ash, fly ash and results in a stable structural-sound end product. The limitations of S/S are the contaminants will diffuse slowly, requires the curing period, can deteriorate over time, requires excavation and materials handling and does not destroy compound (Conner, 1990).

Table 2.4 Advantages and Disadvantages of Various S/S Processes (Conner, 1990)

Process	**Description**	**Advantages**	**Disadvantages**
Cement-based	Slurry of wastes and water is mixed with portland cement to form a solid	Low costs, readily available mixing equipment, relatively simple process, suitable for use with metals	Solids are suspended, not chemically bound and subjected to leaching, doubles waste volume, requires secondary containment, incompatible with many waste
Lime-based	Waste is reacted with lime and a fine grained siliceous material to form a solid	Low cost, readily available mixing equipment, suitable for power plant wastes, as well as a wide range of industrial wastes, including metals, waste oil and solvents	Increases waste volume, may be subjected to leaching, requires secondary containment
Thermoplastic	Waste is dried, heated and dispersed through a heated plastic matrix of asphalt bitumen, paraffin or polyethylene	Less increase in volume, reduced leaching relative to other processes, suitable for radioactive wastes and some industrial wastes	Wastes must be dried before use, high energy and equipment costs, required trained operators, incompatible with oxidizers, some solvents and greases, some salt and chelating/complexing agents, requires

			secondary containment
Organic Polymers	Waste is mixed with a prepolymer and a catalyst that causes solidification through formation of a spomge like polymer matrix. Urea formaldehyde or vinyl ester-strene polymers are used	Suitable for insoluble solids, very successful in limited application	Pollutants are not chemically bound, subject to leaching, strongly acidic leach water may be produced, requires special equipment and operators, some of the catalysts used are corrosive, harmful vapors may be produced, incompatible with oxidizers and some organics, some resins are biodegradable and decompose with time

2.10 LOCAL STUDIES ON S/S TECHNIQUE

There were various local studies on the use of S/S technique. Gai (1994) studied the compressive strength and leaching behaviour of the metal bearing paint sludge from *Perusahaan Otomobil National* (PROTON) using S/S technique. The sludge could be categorized into 3 types;

i. Sludge A - was collected from the surface of the primary sedimentation basin in the painting section.
ii. Sludge B - was designated from the phosphate sludge treatment system.
iii. Sludge C - was designated from sludge A that was burnt under high temperature.

In this study, C/Sd of 0.5, 1, 2, 3 and 4 were used. The results of compressive strength could be plotted in the following graph.

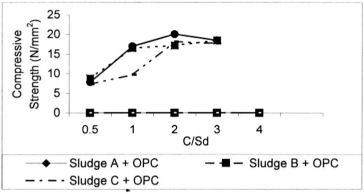

Figure 2.1 UCS development of the PROTON solidified samples for various C/S_d ratios

From the graph, it is obvious that C/S_d is proportional to the compressive strength for all sludge and the strength exceeded the UK Regulation limit of 0.34 N/mm^2. The ranking in terms of highest strength obtained with respect to C/S_d ratio can be ranked as follows;

Sludge A > Sludge B > Sludge C

Leachate analysis for lead, copper and zinc was tested using Graphite Furnace AAS on the basis of parts per billion (ppb). The toxic metals concentration for 0.5M HAc (pH = 2.88) showed a greater value of metal leached compared to DW (pH = 6.7) leachates. It was found that the lead concentration in both HAc and DW leachants of sludge A increased with the increment of C/S_d ratio. For copper concentration, the results indicated that the amount of metal released in DW leachant were almost the same. On the other hand, the copper concentration increased with C/S_d ratio in the HAc leachant. The concentration of zinc in HAc leachant decreased linearly until it achieved the lowest value at C/S_d = 4.

For sludge B, the lead concentration was very low in the leaching medium of DW. The lead concentration was proportional to the amount of sludge added to the stabilized sludge samples. It was found that the amount of copper released from the stabilized wastes was not directly related to the mass of the sludge added in the stabilized materials. The zinc concentration in DW increased with respect to C/S_d ratio but did not show as it was in HAc medium.

For sludge C, it was found that the highest amount of copper leached out from the solidified sludge was at C/S_d = 1 for both mediums. In the HAc leachant, the zinc concentration was not directly related to the C/S_d ratio. As a conclusion from this study, the concentration of lead and copper were below the USEPA Toxicity Regulatory Discharged Limit except for zinc. The concentration of zinc for all the stabilized wastes of sludge B and C in HAc leachant exceeded the regulatory limit while for stabilized samples of sludge A exceeded the regulatory limit at the C/S_d=0.5.

Lim (1993) studied the effectiveness of using methods of S/S as a treatment process for the petroleum sludge. There were two types of sludge used in this study;

i. stored/aged sludge (OGT sludge)

ii. wet sludge from Waste Oil Ex-Kuantan Bulk Depot (wet sludge).

Wet sludge was used for the compressive strength study while OGT sludge was used for the leaching study. In this study, C/S_d of 3, 5, 6 and 7 were used. The findings of UCS could be plotted in the following graph.

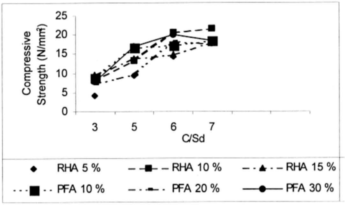

Figure 2.2 UCS development of the petroleum solidified samples for various C/S_d ratios

From the above graph, it was observed that the increment of compressive strength value was not related to the increase of CRM percentage. Cement-sludge paste with 10 % of RHA added indicated a higher strength compared to 5 % or 15 % of RHA. However, the solidified waste cubes with 30 % of PFA gave the highest strength when compared to the samples of 10 % and 20 % of PFA. In conclusion, CRM also could enhance the setting time of cement-sludge paste, improve its durability, minimize interfering organic compounds and simply absorb water.

OGT sludge was used for the leaching study based on C/S_d = 0.25, 0.50, 0.75 and 1.00. In this study, leachate analysis for lead, copper and zinc was tested using Flame Atomic Absorption Spectrometry on the basis of parts per million (ppm). It was found that the amount of lead released in both medium was inversely proportional to the amount of sludge added to the stabilized waste samples. Lead concentration was decreased in each following extraction. The final extraction of leachate presented the lowest lead released from the stabilized waste samples. The decreased of lead concentration was not uniform throughout the subsequent 6 extractions.

Analysis of lead released from the stabilized waste samples indicated that lead extracted throughout the whole subsequent extractions was less compared to lead concentration in the initial sludge. For copper analysis, it was found that copper concentration increased in the first extraction. The copper released was not directly related to the amount of sludge added. The amount of zinc released was directly related to the amount of sludge added to the stabilized samples. It was found that the solidified samples soaked in DW were not severely deteriorated compared to HAc medium. The zinc released was very low and could be hardly detected by FAS. Comparison of zinc concentration presented in leachate and untreated OGT sludge indicated that the leaching of zinc from the stabilized waste samples were not critical or considered as hazardous wastes.

In conclusion, using the two above examples, it was proven that the S/S technique could increase the strength development and reduce the leaching of heavy metals from the solidified samples if compared to the initial metals concentration of untreated waste.

2.11 BINDERS AND BINDING MECHANISMS

Binder systems can be divided into two categories which are organic and inorganic binders. Organic binders are used or experimented with epoxy, polyesters, asphalt, polyolefins and urea foermaldehyde. Most inorganic binding systems include varying combination of hydraulic cements, lime, pozzolans, gypsum and silicates. Combinations of these systems have also been used. These include diatomaceous earth with cement and polystyrene, polyurethane and cement, polymer gels with silicate and lime cement. The most commonly used binders are inorganic such as cement kiln dust, fly ash and other waste of binder which can chemically react with water. In order for S/S process to be effective, the binder used must react with free water in the waste and form a solid, bind with the metals and organics to reduce their chemical nature and/or their leachability, bind with organic air emission in the waste to reduce their chemical nature and ability to vaporize.

2.11.1 Inorganic Binder

The two principal types of inorganic binders are cement binder and pozzolonic binder (lime, kiln dust, fly ash, rice husk ash). A pozzolan is a material containing silica that has a little or no cementation value itself but under some conditions, can react with lime to produce cementitious material. Cement-based and pozzolanic processes or a combination of cement and pozzolans are the method of choice in the S/S industry today. This probably is attributable to the low cost of materials, their applicability to a wide variety of waste types and the ease of operation in the field.

2.12 MATERIALS FOR STABILIZATION AND SOLIDIFICATION

Solidification and stabilization of waste sludge is often accomplished by the addition of a substance that absorbs or react with water and produces a solid. Portland cement is effective for this purpose for many wastes. Pozzolanic materials consisting of hygroscopic silicates, such as those produced in fly ash, is an effective drying agent for solidification process for waste disposal such as cement-based techniques, organic polymers, encapsulation, self-cement techniques and glassification. All these processes need a combination of cement, cement kiln dust, soluble silicates, fly ash, ground blast furnace slag, lime and other proprietary additives are mixed with waste to increase bearing strength, eliminate free liquids and reduce leachability before disposal .

2.12.1 Cement

Cement consists of raw materials mainly of lime silica, alumina and iron oxide. These compounds interact with one another in the kiln to form a series of more complex products, and it is a material that hardens in the presence of water. In the presence of leachability, bind with organic air emission in the waste to reduce their chemical nature and ability to vaporize.

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2.12.1 Cement

Cement consists of raw materials mainly of lime silica, alumina and iron oxide. These compounds interact with one another in the kiln to form a series of more complex products, and it is a material that hardens in the presence of water. In the presence of water, the silicates and aluminates of cement from products of hydration or hydrates, which in time produce a firm and hard mass - the hardened cement paste. The two calcium silicates are the main cementitious compounds in cement, the former hydrating much more rapidly then the latter. In commercial cement, the calcium silicates contain small impurities from some of the oxides present in the clinker. These impurities have a strong effect on the properties of the hydrated silicates. Typical weight proportions in ordinary cement are 50 % C_3S, 25 % C_2S, 10 % C_3A, 10 % C_4AF and 5 % other oxides. There are many types of cement, but only those classified as portland cement have substantial use in S/S technology.

2.12.2 Pozzolanic Materials

Pozzolans are materials that display no cementing actions by themselves but which contains constituents that combine with lime at ordinary temperatures and in the presence of water to form cementitious compounds. Typical materials of this type are volcanic ash, pumicite, opaline shales and chert, calcined diatomaceous earth, burnt clay and fly ash. Pozzolans may often be cheaper than the portland cement but their main advantage lies in slow hydration and therefore low rate of heat development. Hence, partial replacement of portland cement by pozzolan is used in mass concrete construction and solidification of solid waste.

2.12.3 Silicate Materials

Water-insoluble silicates used for waste-solidification include fly ash, flue dust, clay, calcium silicates and ground up slag from blast furnaces. Soluble silicates, such as sodium silicate, may also be used. Silicate solidification usually requires a setting agent, which may be portland cement, gypsum, lime or compound of aluminium, magnesium or iron. The product may vary from a granular material to a concrete-like solid. In some cases the product is improved by additives, such as emulsifiers, surfactant, activators, calcium chloride, clays, carbon and various proprietary materials.

2.13 EFFECTS OF ORGANIC WASTES ON CEMENT/POZZOLAN SYSTEMS

Limited studies are geared towards the effects of typical organic waste constituents upon cement and pozzolan stabilization and solidification process (Jones,1990). Most of these studies did not include extensive testing of the final waste-cement product. Leaching and strengths for the resultant waste-binder are complicated by the fact that the interfering affects can vary with cement- or pozzolan-to-water ratios, interactions with other waste constituents, type, order and duration of mixing.

Effects of organics on the macrostructural properties of cement can be greatly minimized if one understands the microstructural effects of the organics on cement. Phenolic compounds (phenol. 3-chlorophenol and 2,3-dichlorophenol) have shown to have detrimental effects on the macrostructural properties of OPC i.e. effects of strength, setting rate and leachability of cement. Fundamental studies on the interactions of 3-chlorophenol and chloronapthalene with cement matrix demonstrated that 3-chlorophenol crystallized in the cement matrix to form discrete crystals containing phenol and calcium. Chloronapthalene on the other hand do not have an observable effect on the hydration of cement.

Microstructural studies by Sollars *et al.*, (1988) showed that 3-chlorophenol inhibited the hydration of tricalcium silicate while chloronapthalene had no observable effect on cement hydration. 90% of the tricalcium silicate remained after 28 days for the highly dosed 3-chlorophenol/OPC specimen. Concentration of phenol as low as 0.2 % by volume have been found to have an adverse effect on the development of compressive strength of concrete (Smith, 1988). The effect of triethanolamine (TEA) on the setting characteristics of portland cement has been studied by thermogravimetric analysis and conduction calorimetry. It was found that concentration of TEA between 0.17 to 0.5 % will greatly accelerate the initial set but retards the final set, thus producing a weaker cement structure. Studies on the effect of ethylene glycol and p-bromophenol showed that these two compounds altered cement microstructure (Hill *et al.*, 1992). Ethylene glycol samples results in grainy, nodular surfaces which lacked crystallinity.

On the other hand, the p-bromophenol samples showed little deviation from the control samples except at high concentration. It is postulated that this difference arises due to the size of ethylene glycol. The size of ethylene glycol is closer to water thus making it possible to substitute for water during hydration and cause deformation in cement microstructure. The effect of organic compound on the hydration of cement is increasingly being studied by conduction calorimetry (Alloway & Ayres. 1993). Cheeseman *et al.*, (1993) investigated a wide range of inorganic and organic admixtures using isothermal conduction calorimeter and devised comparative ranking system of inorganic and organic admixtures. In general organics mixtures act as retarders of cement hydration.

Information on the effects of organics in pozzolanic systems is limited. Even though pozzolanic reactions are generally slower than the hydration reactions of portland cement, in both cases the strength of the final product results from the formation of hydrated calcium silicates. Organic compounds which inhibit this process can be expected to affect both cement and pozzolanic systems in a similar manner.

2.14 CEMENT SETTING AND HYDRATION

Setting is the term used to describe the stiffening of the cement paste. Setting refers to a change from a fluid to a rigid state. In practice, the terms initial set and final set are used to described arbitrarily chosen stages of setting. It seems that setting is caused by a selective hydration of cement compounds: the two first to react are C_3A and C_3S. The flash-setting properties of C_3A were mentioned in the preceding section but the addition of gypsum delays the formation of calcium aluminate hydrate and it is thus C_3S that sets first. Neat C_3S mixed with water also exhibits an initial set but C_2S stiffens in a more gradual manner (Jones, 1990).

In a properly retarded cement, the framework of the hydrated cement paste is established by the calcium silicate hydrate, while if C_3A were allowed to set first a rather porous calcium aluminate hydrate would form. The remaining cement compounds would then hydrate within this porous framework and the strength characteristics of the cement paste would be adversely affected. The setting process is accompanied by temperature changes in the cement paste: initial set correspond to a rapid rise in temperature and final set to a peak temperature. The setting time of cement decrease with a rise in temperature, but above 30 ^{0}C a reverse effect may be observed. At low temperature setting is retarded.

The hydration of portland cement is a series of simultaneous and consecutive reaction between water and solid cement constituents which occur in the setting and hardening processes. Dispersing portland cement in water causes the various constituents to go into solution, which rapidly saturates the liquid phase with the various ionic species. The first needle-like crystals of calcium sulfoaluminate hydrate (ettringite) appear within a few minutes of cement hydration. After a few hours, large prismatic crystals of calcium silicate hydrates (C-S-H) begin to fill the empty spaces formerly occupied by water and the dissolving cement particles. The most important reactions in later stages are the hydration of calcium silicates that continues for many months at decreasing rates.

Strength development after setting is primarily due to C_3S and C_2S, both of which give the same reaction products, that is, calcium hydroxide (CH) and calcium silicate hydrate, or tobermorite gel (C-S-H). The reaction of hydration of both C_3S and C_2S can be written as follows:

For C_3S :

$$2C_3S + 6H \longrightarrow C_3S_2H_3 + 3CH$$

For C_2S :

$$2C_2S + 4H \longrightarrow C_3S_2H_3 + CH$$

Thus on a weight basis both silicates require approximately the same amount of water for their hydration, but C_3S produces more than twice as much calcium hydroxide (CH) as is formed by the hydration of C_2S. The presence of significant amounts of CH makes the concrete reactive to acidic solutions. The amount of C_3A in most cement is comparatively small and 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.

Hydration of C_3A in the absence of sulfate ions can be represented by the following equation (Jones, 1990):

$$2C_3A + 21H + C_4AH_{13} + C_2AH_8 \longrightarrow 2C_3AH_6 + 9H$$

The heat liberated in above equation is sufficient to speed up the reaction to the stable form, C3AH6. However, Portland cement does contain a small amount of sulfate as gypsum. If sufficient sulfate is present, C3A and sulfate react almost immediately to form hydrated calcium aluminate sulfate (ettringite), which coats the surfaces of the particles, preventing rapid further hydration. This is why gypsum retards setting.

The reaction is as follows;

$$C_3A + 3CSH_2 + 26H \longrightarrow C_3A.3CS.H_{32}$$

The addition of 26 water molecules during the formation of ettringite brings about a corresponding volume increase. When ettringite forms early in the solidification process, the additional space is not a problem, it evens develops binding properties that contribute to the early strength of the product. This phenomenon can actually be used to bind large amounts of sulfate in a solidification product by using clay-rich (alumina) binders. However, if the ettringite forms after solidification, the additional space required loosens the structure and causes an observable increase in permeability with a concomitant loss in strength. After a period of time, the length of which depends on the alumina-to-sulfate ratio of the cement, the ettringite crystals may react with C_2A according to :

$$4H + 2C_2A + C_3A.3CS.H_{32} \longrightarrow 3C_3A.CS.H_{32} + 4H$$

Monosulfoaluminate in portland cement concrete makes the concrete vulnerable to sulfate attack. Davis & Cornwell (1991) hypothesized that the effect of organic compounds on the hydration of cement depends on their interaction with the hydration products rather than the anhydrous cement. Double (1984) employed conduction calorimetry to classify the effect of a range of organics on cement hydration. The retarding efficiency has generally been found to increase with the molecular weight. Many inorganic electrolytes are capable of accelerating the hydration of tricalcium silicate with the exception of fluorides, phosphates and cations that precipitate as hydroxides. Studies have shown that the early hydration of cement were modified by the incorporation of heavy metals (Montgomery et al., 1988). Another effect of heavy metal to the cementitious matrices is to enhance the formation of calcium sulphoaluminate.

2.15 CEMENT REPLACEMENT MATERIALS

Cement is in high demand these days, because of rapid development in our country for the concrete building construction industry. This has a direct consequence on the price increase and the shortage in the cement market. The ideal features are to replace cement with other materials, which have closer similarity characteristic and the chemical contain in the cement (Scar,1998). The materials that can be used as the replacement materials are fly ash, rice husk ash, condensed silica fume, pozzolanic material (volcanic ash), pumicite and etc.

2.15.1 Pulverised Fly Ash (PFA)

PFA is a by-product from the combustion of pulverised bituminous coal in electric power generation. The ash is collected from the furnace gases by a combination of mechanical filtration and electrostatic precipitators. The use of PFA as partial substitute for commercial binders, mainly portland cement, in the S/S of metal containing wastes has been widely considered. PFA is composed primarily of silica, alumina, iron oxide and calcium oxide. Physically, fly ash consists of finely divided spheroids of siliceous glass, about 1 to 50 microns in diameter, plus minor fractions of larger, irregularly shaped particles. These particles act like ball bearings within the concrete, reducing the water requirement for a given workability. Reducing the water content lowers the permeability and increases strength and durability. In addition, the concrete is more cohesive, has a lower rate of bleeding and is less prone to segregation (Keck & Riggs, 1997).

PFA has both pozzolanic and physical properties that enhance the performance of concrete. However, the PFA is a pozzolanic material possessing no cementitious properties of its own but able to react with the lime liberated during the hydration of calcium silicate in cement to produce calcium silicate. When portland cement hydrates, it produces quantities of calcium hydroxide (lime). PFA reacts with lime to form stable calcium silicate and aluminate hydrates which reduce the voids within the concrete, removing some of the lime and so reducing the permeability. The pozzolanic reaction occurs slowly at normal temperatures, further enhancing strength in the longer term relative to normal portland cement concrete (Scar, 1998).

2.15.2 Rice Husk Ash (RHA)

Rice hush ash containing silica in a highly reactive form is found to be an excellent ingredient for making hydraulic blended cement. The RHA is produced by burning the rice husk under two different methods, which are, open burning and laboratory burning. The chemical reactivity of the ash, particularly in combination with lime is related to the form of silica in the ash and the carbon content. In the portland cement, RHA mixtures, the surface of the RHA particles become coated with a C-S-H product as the hydration commerce. The main components in the RHA are lime, silicate, aluminate and iron oxide. The quantity of SiO2 is very high in the RHA and its presence influences the atomic arrangement in the form of crystal and also influences the characteristic of hydraulic silicate. The existence of alkalinity quantities in the RHA is little and it is more or less the same amount as in the OPC.

2.16 HEAVY METALS

Inorganic substances are widely manufactured and used industrially. Numerous inorganic substances occur in waste materials. Although any element may be a constituent of hazardous wastes, usually in a combined form, some elements tend to predominate in wastes. These elements are usually classified as hazardous because of the toxicity of their elemental forms or compounds. Some metals, commonly known as heavy metals, are particularly toxic in their chemically combined forms, notably in the case of mercury and some are toxic in the elemental form or compounds. Toxic metals are harmful to humans and other organisms in small quantities. Toxic metals that may be dissolved in water include arsenic, barium, cadmium, lead, mercury and silver. Cumulative toxins such as arsenic, cadmium, lead and mercury are particularly hazardous. These metals are concentrated by the food chain, thereby passing the greatest danger to organisms near the top of the chain (Shiverly *et al.*, 1986).

The danger of exposure to lead is higher than that for many other toxicant because it is widely distributed as metallic lead, inorganic compounds and organometallic compounds. Lead has a number of toxic effects, including inhibition of the synthesis of hemoglobin. It also adversely affects the central and peripheral nervous systems and the kidneys. Copper is relatively abundant in minerals and soils. The metal is required for all forms of aerobic life and most anaerobic forms. No chronic poisoning has been reported in humans, although ingestion of very large amounts can cause temporary systematic effects. Zinc is found in all natural waters and soils, and is an important nutrient in plant and animal life. Zinc is not toxic to humans, it is used as a dietary supplement and animals have a high tolerance for it. It is necessary for plant growth, but very high levels can cause toxic effects.

Arsenic is a metalloid which forms a number of toxic compounds. The toxic 3^+ oxide, AS_2O_3, is absorbed through the lungs and intestines. Biochemically, arsenic acts to coagulate proteins, forms complexes coenzymes and inhibits the production of adenosine tri-phosphate (ATP) in essential metabolic processes. Cadmium adversely affects several important enzymes and it can cause painful osteomalacia (bone disease) kidney damage. Inhalation of cadmium oxide dust and fume results in cadmium pneumonitis characterized by edema and pulmonary epithelium necrosis.

2.17 PREVIOUS STUDIES ON UNCONFINED COMPRESSIVE STRENGTH (UCS)

Some previous studies have been carried out to examine the S/S treatment process in heavy metal sludge by using OPC and PFA (Ibanez et al., 1998, Hills *et al.*, 1992, Montgomery *et al.*, 1988, Scar, 1998). The strength development has been observed. From the studies, it was found that the compressive strength increased with each increment of C/S_d ratio. The results of compressive strength for all the treated waste were satisfied the UK regulatory limit for solidified specimen with a value of 0.34 N/mm^2.

2.18 LEACHING MECHANISMS

Heavy metals solidified and stabilized with ordinary Portland cement which form a cement paste (cement mixed only with water sets to form cement paste) are referred as stabilized waste. Cement paste is highly alkaline with silica oxyhydroxide surfaces that provide an environment for amphoteric metal precipitation and complex sorption reactions. Water decomposes cement paste by dissolving lime and some alumina. Continued leaching leaves a residue of hydrated silica, iron oxide and alumina. This reaction is negligibly slow with most natural waters, but much faster with acidic solutions. This action progressively weakens the materials because constituents are removed and soft mushy silica-rich solids remain.

2.18.1 Previous Studies on Leaching

Several surveys, studies and reviews of existing processes have recently been carried out by researchers (Chung, 1994, Cheeseman *et al.*, 1993, Wiles & Barth, 1990),. The treatment decreases waste leachability and has the potential to detoxify the hazardous constituents in the waste. A study of the release of isotopes from cement stabilized radioactive wastes indicated that diffusion is one of the limiting mechanisms. Diffusion modelling has been applied to the results of leaching process when leachate concentration does not reach equilibrium. Acid attacks cement through permeation of pore structure and dissolution of ions that must diffuse back through a chemically altered to enter solution.

From the researchers investigation, it showed that the results of single extractions could present a very different picture of materials decomposition when compared to the results of sequential tests. Leaching tests should provide information about the behaviour and mobility of wastes disposed in the environment. The research reported that leachate analysis showed the release of heavy toxic metals and cement paste degradation but its constituents passed the EPA EP-toxicity test and are not considered hazardous waste.

2.18.2 Toxicity Characteristic Rules

Over the past few years, a need for basic information on more definitive testing and regulation for hazardous materials in the environment has emerged. Regulatory and enforcement agencies at all levels of government agree that technically sound measurement systems and characteristic rule must be developed on a national scale to ensure that both the regulators and the regulated are measuring and testing in the same manner. Here the assessment are mostly referred to US Environment Protection Agency (EPA), as it established a new section of RCRA that the criteria used to list a hazardous waste be expanded include additional chemicals. In response, EPA proposed a revised leachate procedure referred to as the Toxicity Characteristic Leaching Procedure (TCLP) and added 39 chemicals to the environment pollutant (EP) list. The rule has been referred to as the Toxicity Characteristic (TC) rule. This rule supplements the EP toxicity rule by adding 25 new chemicals to the list of wastes having regulatory levels above which a waste becomes a characteristic hazardous waste.

2.19 LEACHING TESTING

Leaching of metals can be evaluated by a number of methods.

2.19.1 Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphasic wastes. If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run. If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for the compound, then the waste is hazardous and it is not necessary to analyse the remaining fractions of the extract. If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for the compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.19.2 Synthetic Acid Precipitation Leach Test (SAPLT)

The Synthetic Acid Precipitation Leach Test is similar to the TCLP but the initial liquid-to-solid separation step has been eliminated and the acetate buffer extraction fluid has been replaced by a dilute nitric acid or sulfuric acid mixture. This test simulates acid rain as opposed to simulating a leachate in a sanitary or municipal landfill.

2.19.3 Shake Extraction Test (SET)

The Shake Extraction Test is applicable only to inorganic compounds, which involves the extraction of a solid waste with reagent water in a rotary agitator for 18 hours. This procedure is intended as a rapid means of obtaining an aqueous extract and is not intended to simulate site-specific leaching conditions.

2.19.4 Sequential Leach Test (SLT)

The Sequential Leach Test is used to evaluate the waste buffering capacity and alkalinity of cement-based stabilization and solidification treated waste. Unlike acid neutralization capacity, the SET involves 15 sequential extractions of one sample of crushed waste with particle sizes between 2.0 mm and 9.5 mm. Each extraction is performed on a shaker table for 24 hours with the same type of extraction solution (0.04M acetic acid solution) and liquid-to-solid ratio of 50:1

2.19.5 Sequential Chemical Extraction (SCE)

This test was developed specifically to evaluate the species of organic and inorganic waste constituents in a stabilized matrix. Like SET, the test involves sequential extraction of the sample. Unlike SET, the leaching solution increases in acidity from neutral to very acidic with each sequential extraction. The particle size of the sample is also very small (less than 45um) and the sample is agitated on a Burrell wrist-arm shaker.

2.19.6 Multiple Extraction Procedure (MEP)

Although MEP is not a regulatory leaching test, it has been used in some instances for delisting wastes. This test involves multiple extractions of the crushed sample with a synthetic acid rain solution. The results obtained by MEP can be used to determine maximum leachate concentrations occuring under acidic conditions.

2.19.7 Monofilled Waste Extraction Procedure (MWEP)

Formerly it is called the Solid Waste Leach Test (SWLT). MWEP involves multiple extractions of a monolith or crushed waste with distilled water. This test can be used to derive reasonable leachate compositions in monofilled disposal facilities and this information can be used to assess water-liner compatibility under mild leaching conditions.

2.19.8 Equilibrium Leach Test (ELT)

This leach test involves static leaching of hazardous constituents in distilled water. The ELT can be used to determine maximum leachate concentrations under mild leaching conditions. The leachate concentrations from the two tests (ELT and MWEP) should be comparable if equilibrium conditions are achieved under both. Sample heterogeneity and analytical limitations may cause differences.

2.19.9 American Nuclear Society Leach Test (ANSLT)

The American Nuclear Society Leach Test is applied to stabilized/solidification low-level and hazardous wastes. A monolith cylinder is leached with demineralized water applied at a V/S ratio of 10 cm under ambient temperatures. At the start of the experiment, the sample is rinsed to obtain zero contaminant concentration at the surface of the sample. Afterwards the sample is immersed in water, which is replaced after 2 hours, 7 hours, 24 hours, 48 hours, 72 hours, 4 days, 5 days, 14 days, 28 days, 43 days and 90 days.

2.19.10 Dynamic Leach Test (DLT)

The Dynamic Leach Test is a modified version of the ANSLT. The only modification to the leach test is the renewal frequency of the leaching solution and the V/S ratio, which is based on known coefficients and the results from the batch extraction test.