CHAPTER 2 LITERATURE REVIEW

2.1 INTRODUCTION TO ELECTRONIC INDUSTRY

The production of electrical and electronic equipment is one of the fastest growing domains of manufacturing industry in the world. Technological innovation and market expansion accelerate the replacement process and new applications of electrical and electronic equipment are increasing significantly. Therefore the resulting rapid growth of waste from this industry is of concern.

The hazardous contents of this industry cause high concern when these products become waste, since these are not separately collected and pre-treated and end up in municipal waste landfills where appropriate measures for preventing the hazardous substances from entering into the environment are missing.

Global environmental issues have been brought about with the expansion of human activities and are related to everyday social activities. The electronic and electrical industries have a very close relationship with such global environmental issues, because of their products, which are being utilized in everyday human life, and because of their production processes. The production of electric and electronic equipment is one of the fastest growing areas. This development has resulted in an increase of waste electric and electronic equipment. In view of the environmental problems involved in the management of electric and electronic waste, many countries and organizations have drafted national legislation to improve the reuse, recycling and other forms of recovery of such wastes so as reduce disposal.

The relationship of environmental issues with the electronic and electrical industries begins with the traditional activity of prevention of the pollution and the contamination which production processes generate in the area close to their facilities. The relationship is found in such area as the prevention of harmful effects on the global environment which production activities cause extensively around their facilities and, moreover, in the reduction of the impact the products have on the global environment, both during and after use. Recently, such a relationship has been observed in the development of technologies and in the manufacturing of products which contribute to the prevention of reduction of pollution in the global environment (McGrath, 2001).

2.1.1 Product Characterization

Semiconductors

Although semiconductors account for only a small portion of electronics industry sales, this product is crucial to all electronic products and the United States (US) economy. Semiconductors can serve one of two purposes : they act as a conductor, by guiding or moving an electrical current; or as an insulator, by preventing the passage of heat or electricity. Semiconductors are used in computers, consumer electronic products, telecommunication equipment, industrial machinery, transportation equipment and military hardware. Typical functions of semiconductors in these products include information processing, display purposes, power handling, data storage, signal conditioning and conversion between light and electrical energy sources (Chang, *et al.*, 2002).

Printed Wiring Boards (PWB)

Computers are also the major US market for PWBs, with communications being the second largest application market. The Institute for Interconnecting and Packaging Electronic Circuits (IPC) indicates that nearly 39% of printed wiring boards produced in 1993 were used by the computer market, while 22% were used by the communication industry. PWBs and assemblies are used in many electronic products such as electronic toys, radios, television sets, electrical wiring in cars, guided-missile and airborne electronic equipment, computers, biotechnology, medical devices, digital imaging technology and industrial control equipment (Chang, *et al.*, 2002).

Cathode Ray Tubes (CRT)

According to EPA's Common Sense Initiative (CSI) subcommittee, the CRT industry produces tube glass, colour picture tubes and single phosphor tubes, television sets and computer displays. Currently nearly all projection television tube and computer display manufacturers and the majority of CRT glass manufactures are located outside the US. Therefore, this CRT industry profile focuses on the production of colour picture tubes, single phosphor tubes and rebuilt tubes. These products are the video display component of television, computer displays, military and commercial radar and other display devices (Chang, *et al.*, 2002).

2.1.2 Industrial Processes in the Electronics Industry

1) Semiconductor

Semiconductors are made of a solid crystalline material, usually silicone, formed into a simple diode or many integrated circuits. A simple diode is an individual circuit that performs a single function affecting the flow of electrical current. Integrated circuits combine two or more diodes. Up to several thousands integrated circuits can be formed on the wafer, although 200-300 integrated circuits are usually formed. The area on the wafer occupied by integrated circuits is called a chip or die.

The semiconductor manufacturing process is complex and may require that several of the steps be repeated to complete the process. To simplify this discussion, the process has been broken down into five steps :

i) Design
ii) Crystal processing
iii) Water fabrication
iv) Final layering and cleaning
v) Assembly

The primary reason that semiconductors fail is contamination, particularly the presence of any residue (including chemicals or dust) on the surface of the base material or circuit path. Therefore, a clean environment is essential to the manufacture of semiconductors. Cleaning operations precede and follow many of the manufacturing process steps. Wet processing, during which semiconductors devices are repeatedly dipped, immersed, or sprayed with solutions, is commonly used to minimize the risk of contamination

2) Printed Wiring Board Manufacturing

Printed wiring boards (PWBs) are the physical structures on which electronic components such as semiconductors and capacitors are mounted. The combination of PWBs and electronic components is an electronic assembly or printed wiring assembly (PWA). PWBs are subdivided into single-sided, double-sided, multilayer, and flexible boards. Multilayer boards are manufactured similarly to single and double-sided boards, except that conducting circuits are etched on both the external and internal layers. PWBs are produced using three methods : additive, subtractive or semi-additive technology. The subtractive process accounts for a significant majority, perhaps 80%, of PWB manufacturing. PWB manufacturing can be grouped into five steps :

i) Board preparation
ii) Application of conductive coatings (plating)
iii) Soldering
iv) Fabrication
v) Assembly

3) Cathode Ray Tube Manufacturing

Cathode Ray Tubes (CRTs) have four major components : the glass panel (faceplate), shadow mask (aperture), electron gun (mount), and glass funnel. The glass funnel protects the electron gun and forms the back end of the CRT. In response to electrical signals, the electron gun emits electrons that excite the screen. The shadow mask forms a pattern applied through one of several kinds of photolithography. The process is grouped into six steps (USEPA, 1995):

i) Preparation of the glass panel and shadow mask
ii) Application of the coating to the glass panel interior
iii) Installation of the electron shield
iv) Preparation of the funnel and joining to the glass/shadow mask assembly
v) Installation of the electron gun
vi) Finishing

2.1.3 Raw Materials Inputs and Pollution Outputs

Electric and electronic industry waste is non-homogeneous and complex in terms of materials and components. It consists of a large number of components of various sizes and shapes, some of which contain hazardous components that need be removed for separate treatment. Rinse water originates from several steps in the manufacturing process for electronic devices. The production of printed circuit boards (PCB) can be used as an example. The various steps in the manufacture of components in the electronics industry which give rise to rinse water can be classified as follows (USEPA, 1995) :

i) Cleaning: Removal of oil, grease, cooling fluids and other contaminants generated by mechanical shaping. The relative water solutions contain surfactants, inorganic salts and various additives. Major components are inorganic acids or alkali hydroxide, surfactants, corrosion inhibitor, complexing agents, phosphates, silicates, borates, etc.

ii) Etching: Removal of parts of the products. Major components are acid aqueous solutions containing various additives such as brighteners, corrosion inhibitor, etc.

iii) Layer deposition/removal: Complete or partial (residual parts) elimination of the layers produced by galvanic, lacquering and wet or dry coating (CVD, spinning) techniques. Major components are complexing agents, organic solvents and developers, wetting agents, brighteners, corrosion inhibitor, organic stripping agents, lacquer residue, polymers, etc (USEPA, 1995).

The rinse water in electronics industry thus usually contains several classes of chemicals such as (USEPA, 1995) :

(i) organic acids (methane sulfonic acid, *p*-toluensulfonic, formic, acetic and citric acids, etc.)

(ii) organic bases (triethanolamine, thiourea, amines, etc.)

(iii) surfactants (polyglycol ether, alkyl benzene and alkane sulfonates, α-sulfo fatty acid esters, soap, fatty alcohol polyglycol ether, ethoxylated fatty amines, etc.),

(iv) organic solvents and developers (alcohols, resorcinol, γ-butirrolactone, formaldehyde, ketones, etc.)

(v) inorganic chemicals such as acids (HNO_3, H_2SO_4, HBF_4, HCl, etc.), salts (K-citrate, NaF, NH_4Cl, etc.), metals (Cu, Sn, Ni, Pb, etc.)

(vi) complexing and wetting agents (cyanides, tartrate, polyethylene oxide), etc.

The composition is thus quite complex with several classes of compounds with different chemical properties. Furthermore, the composition may change with time depending on the specific type of production. In addition several of the chemical present in the rinse water are non-biodegradable or 'recalcitrant'.

All streams are usually sent to a first rinse water bath for primary treatment such as recovery of metal ions and then to a second rinse water bath from which after dilution and eventual post-treatment it is discharged. In the option of recycle, the rinse water from the second bath, after the necessary treatments, is sent to the deionization unit to reduce tap water consumption and cost of its further treatment to reach the required quality.

The cost of the deionization process is the largest in the overall cost of process water for cleaning treatments in the electronics industry and thus a reduction of its cost is the critical issue for process economics. Furthermore, a considerable part of the organics contained in the rinse water are non-biodegradable or `recalcitrant' chemicals (i.e. of difficult conversion) and thus their elimination before emission into surface water is necessary. This post-treatment unit is also a not-negligible part of the global cost of water management.

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The recycle of rinse water therefore can be an economic opportunity. Ojima et al.(1995) estimated the cost of water for semiconductor fabrication in Japan and concluded that in the case of water recycle the running and fixed capital costs can be reduced to about 70% of the original cost in the absence of water recycling. Similar estimations in the case of printed circuit board manufacture in Europe lead to comparable values. Thus, water recycle can be not only a benefit for the environment and natural resources, but also can be an economical opportunity to decrease the cost of water management. In addition, the possibility of better control of water quality leads to better control of water management and thus to higher standards of quality in the production. Table 2.1, 2.2 and 2.3 shows the different product's pollution output.

Table 2.1
Semiconductor Pollution Outputs

Process	**Process Wastes (Liquid/Waste Waters)**	**Other Wastes (Solids)**
Crystal Preparation	Spent deionized water, spent solvents, spent alkaline cleaning solutions, spent acids, spent resist material	Silicon
Wafer Fabrication	Spent solvents, spent acids, aqueous metals, spent atchant solution and spent aqueous developing solutions	Not available
Final Layering and Cleaning	Spent deionised water, spent solvents, spent acids, spent etchants, spent aqueous developing solutions, spent cleaning solutions, aqueous metals	Spent solvents
Assembly	Spent cleaning solutions, spent solvents, aqueous developing solutions.	Spent epoxy material and spent solvents

Source : USEPA (1995)

Table 2.2
Printed Wiring Board Pollution Outputs

Process	**Process Wastes (Liquid/Waste Waters)**	**Other Wastes (Solids)**
Board Preparation	Spent acids and spent alkaline solutions	Sludge and scrap board material
Electroless Plating	Spent electroless copper baths, spent catalyst solutions, spent acid solutionss	Waste rinse water and sludges from waste water treatment
Imaging	Spent developing solutions, spent resist material, spent etchants, spent acid solutions and aqueous metals	Sludges from waste water treatment
Electroplating	Spent etchants, spent acid solutions, spent developing solutions, spent plating baths	Not available

Source : USEPA (1995)

Table2.3
Cathode Ray Tubes Pollution Outputs

Process	Process Wastes (Liquid/Waste waters)	Other wastes (Solids)
Preparation of the Panel and Shadow Mask	Spent solvents	Glass (lead) from breakage
Application of Coating to Panel Interior	Spent photoresists, deionized water, acids, oxidizers, carbon slurry, surfactants, chromate, phosphor solutions, chelating agents, caustics, solvents, alcohol, coatings, ammonia, aluminium and process cooling waters	Lacquer wastes
Installation of Electron Shield	Electron shield degrease and0 metals	Not available
Preparation of Funnel and Joining to Panel-Mask Assembly	Funnel wash, seal surface cleaning, and frit application wastewaters	Frit contaminated clothing instruments, utensils, unusable frot glass (lead), glass (lead) from break-age
Installation of Electron Gun	Spent solvents and caustic cleaners	Glass from breakage

Source : USEPA (1995)

2.1.4 Hazardous Waste

Hazardous waste is also referred to as scheduled waste, special waste, toxic waste or sometimes more specifically, as chemical waste. There is no consensus in the definition and classification of hazardous waste and hazardous material and hence, at times, it causes unnecessary confusion among world nations, especially in waste qualification and transboundary movement.

Generally, a hazardous waste or chemical is a material that is potentially dangerous to human health and causes physical hazards. A more comprehensive definition is given by the World Health Organization (WHO), which states that a hazardous waste is one possessing physical, chemical or biological characteristics, one which requires special handling and disposal procedures to avoid risk to health and/or adverse environmental effects (Agamuthu, 2001). In Malaysia, the waste is classified under scheduled waste if the parameter of the effluents is more than Standard A or Standard B (Environmental Quality Act 1974).

Characteristics of Hazardous Waste

Four features typically associated with hazardous waste are

i. ignitability

ii. corrosivity

iii. reactivity and

iv. toxicity

Chemicals cause a wide range of hazards including health hazards and physical hazards. Thus, another form of classification is based on the type of hazard caused is showed in Table 2.4.

Table 2.4
Hazardous characteristics of chemicals

Health hazards	Physical hazards
1. Carcinogenic	1. Combustible liquids
2. Toxic chemicals or highly toxic chemicals	2. Water reactives
3. Reproductive toxins	3. Flammables
4. Irritants	4. Explosives
5. Hepatoxins (liver)	5. Oxidisers
6. Corrosive chemicals	6. Pyrophorics
7. Neuorotoxins (nervous systems)	7. Compressed gases
8. Sensitisers	
9. Nephrotoxins (kidneys)	
10. Agents that damage the blood, lungs, eyes, or skin	

Sources : Agamuthu (2001)

2.2 WASTE MINIMIZATION

2.2.1 Definition of Industrial Waste

Goodrich (1994) defined waste as the material purchased that is not consumed by customers, and it is used for activities which do not add value to the service rendered to the customers. Besides the regulatory and formal definition, according to Smith (1997), waste can be simply characterized as "material or energy which, in the eye of the producer, arises at a rate and form such that it has no value".

Thus, waste materials include :

- raw materials left in drums or sacks
- fugitive spillage and associated cleaning materials
- fugitive emission/evaporation
- gaseous discharges
- contaminated materials
- off-specification products and
- obsolete or redundant stock of raw materials, intermediate or final products

2.2.2 Design

Waste minimization concerns first, changes or considerations in design which will reduce the amount of waste, bearing in mind that newly-built manufacturing lines are generally rather more waste efficient than retrospectively adapted facilities. Secondly, waste minimization involves improving operating practices so as to reduce product and fugitive waste (UNEP 1994).

The first step in design of waste minimization is an evaluation of existing processes or unit operations in order to identify problem areas in terms of fugitive and process waste production (UNEP 1994).

Waste minimization option can be divided into : source reduction options, that is, any activity that reduces the amount of waste generated in the process; and recycling options, where waste streams can be re-used in the same process or other processes or some components of the waste stream can be reclaimed, thus reducing final waste load (UNEP 1994).

Source reduction activities include product changes, process input or raw material changes, process or technology changes, material substitution and conservation and changing operation practices (UNEP 1993). Figure 2.1 illustrates the different aspects of a waste minimization program.

2.2.3 Cost Associated with Wastes

Goodrich (1994) has described the various consequences of waste generated which is related to material and energy cost, product quality, machinery capacity and environmental compliance. Clark (1995) has further elaborated the various aspects associated with waste generation by using an inter-related web, as illustrated in Figure 2.1. Obviously, some aspects go far beyond pure monetary consideration. It extends over the activities and future viability of an industry.

Any costs incurred due to the waste produced during the production process – excess raw material costs, administration costs associated with transportation, storage and disposal costs must be considered as part of the production costs. In addition, the consequences of unnecessary third-party liability costs and the costs related to remedying improperly disposed hazardous materials, unnecessary depletion of natural resources, generation of poor customer relationship and causing negative public image, lead to the ultimate inevitable loss of business to those more efficient producers who have taken such factors into account (Dowie, *et al.*, 1998).

2.2.4 Benefits of Waste Minimisation

Although the implementation of waste minimization project may require some additional investment in the initial stage, it can provide long-term benefits in various aspects as demonstrated in Figure 2.2. The immediate benefit would be lower waste disposal costs and higher production, whereas, the most important benefit would be the reduced impact on the environment. A better public relations and a secure business climate are the other benefits.

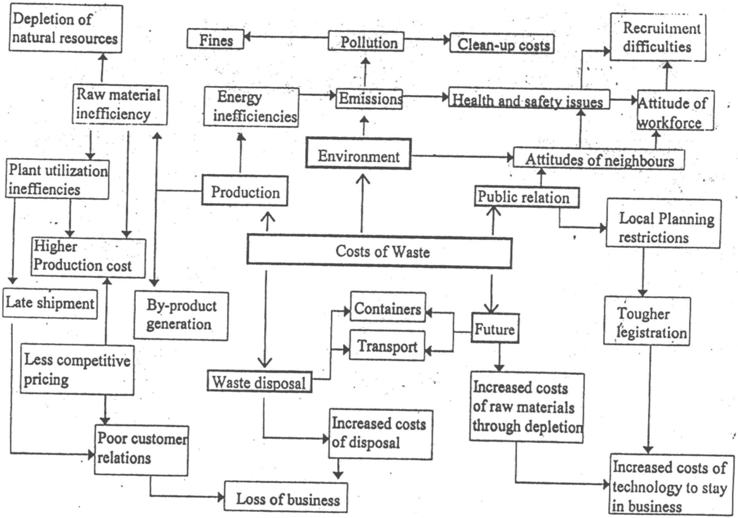

Figure 2.1 Various aspects of costs incurred from waste generation (Clark, 1995)

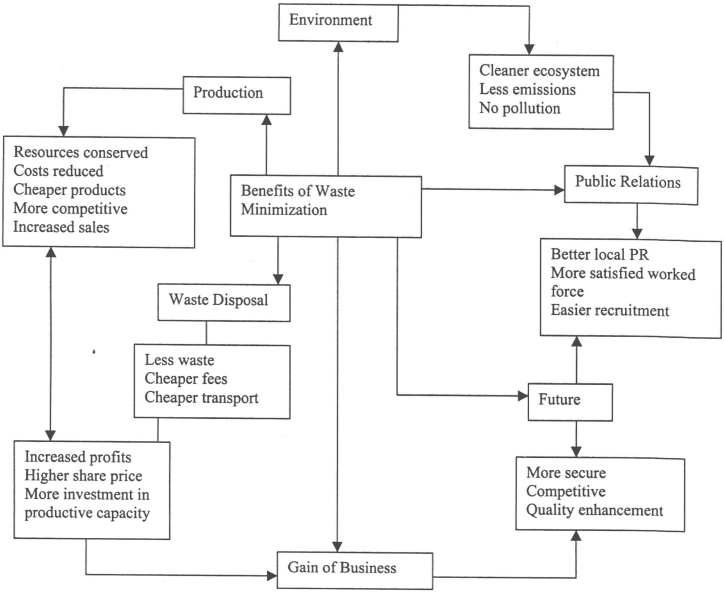

Figure 2.2 Various benefits accrued from implementation of waste minimization program (Clark, 1995)

2.2.5 Developing and Implementing Waste Minimization Program

US EPA (1988) developed a systematic, planned procedure of waste minimization which is suitable and applicable to all types of industries and processes. This procedure was further improved by Crintenden and Kolaczkowski (1995). Petek and Glavic (1996) proposed an integral approach which includes research at all levels of production in a company (organization, maintenance, process, production, distribution and utilization of energy) including optimization after changing environmental and economic conditions. In addition, Slater, *et al.* (1995) also proposed a method that can be used to analyze chemical process flowsheets for waste minimization options and pollution prevention index (PPI) that emphasizes EPA pollution prevention priorities.

A stepwise procedure to develop and implement a waste minimization program is outlined in Figure 2.3 (Hunt and Schecter, 1995). This procedure is suitable for all types and sizes of industries and flexible to be altered to meet local needs.

Obtainment of top management commitment, setting of realistic goals and timescales which are consistent with the policies adopted by top management at the beginning of the project are the key elements to a successful waste minimization program. A careful review of the plant's operations and waste streams are essential to develop options for reducing the types and amounts of waste generated. Then, technical and economical feasibility are selected for implementation (Hunt and Schecter, 1995; Petek and Glavic, 1996).

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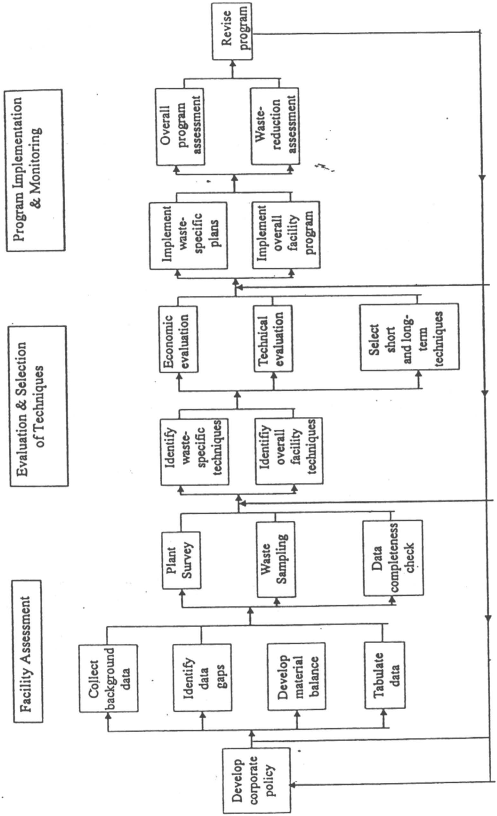


Figure 2.3 Approach of developing and implementing a waste minimization program (Hunt & Schecter, 1995)

2.3 WASTE AUDIT

The essential steps successfully achieving the goal of waste minimization begins with a waste audit (USEPA, 1990; LaGrega, *et al.*, 1994; Sastry, 1995; Shen, 1995). A formal waste audit examines each operation that generates waste to determine how the waste is generated, what are the characteristics, how it is managed and what are the associated costs. This provides baseline condition for evaluating progress towards meeting waste minimization goals. It also provides necessary data to priotize waste streams and to identify alternative options for minimizing the high-priority wastes (LaGrega, *et al.*, 1994). This prioritization is generally based on composition, quantity, costs of disposal, degree of hazard, potential for minimization, recyclability and compliance status (Haas, 1995).

Various versions of waste audit have been established, however there are a few basic elements that are relevant to most of the waste generation scenarios (Mahwar, *et a.l*, 1997). A typical waste audit would comprise the following key components :

Step 1 : Identify the amounts and types of hazardous substances in wastes and emissions, including both regulated and unregulated,

Step 2 : Identify the specific production sources of the wastes and emissions,

Step 3 : Set priorities for waste reduction action on the basis of costs, environmental concern, worker health and safety, liabilities and production constraints,

Step 4 : Analyze and select technically and economically feasible reduction techniques,

Step 5 : Compare the economics of waste reduction alternatives with current and future waste management or pollution prevention options, and

Step 6 : Evaluate the progress and success of chosen waste reduction measures.

Mahwar, *et al.* (1997) also suggested 4 stages of waste reduction audit (WRA) defined by the needs of waste reduction over time and to assess the applicability and scope of WRAs :

Stage 1 : Common Sense Waste Reduction

Immediate reduction opportunities that are readily visible, common sense and low cost are identified through direct observation of the operating process. There are no technical barriers and it can be implemented in days and weeks. They often involve changes in procedures rather than changes in production technologies and major equipment. For examples, improving inventory controls, ceasing the commingling of hazardous with non-hazardous waste and reducing the amount of water consumed in cleaning equipment. This approach could stimulate waste reduction activities, educate production staffs and provide a record of actions and results.

Stage 2 : Information-Driven Waste Reduction

This stage of waste reduction is relatively easy, quick, low cost, and no significant technological obstacles; but it does require more detail information about the generation of waste. Normally, it involves simple changes in production which is prompted by production from similar successful industries. For example, replacing an organic solvent with a water-based solvent and installing a close-loop recycling unit.

Stage 3 : Audit Dependant Waste Reduction

A formal waste audit is critical in this stage, where some technological obstacles are identified and technical and economical feasibility need to be studied. More capital investment become necessary and risk increases due to the uncertainty about economic payback and technical feasibility.

Stage 4 : Research & Development Based Waste Reduction

Extensive research and development (R & D) on process technology or equipment and possibly product composition or design is required in this stage. Some circumstances like large waste stream from well established processes and wastes that seem inevitable unless a different product is design are favor a R & D effort. Careful and continuing economic analysis are required, including economic spin offs and drawbacks should be thought at the outset of the waste minimization. Waste reduction audit need to be carried out periodically for both the original situation and any new waste generating activity resulting from the R & D.

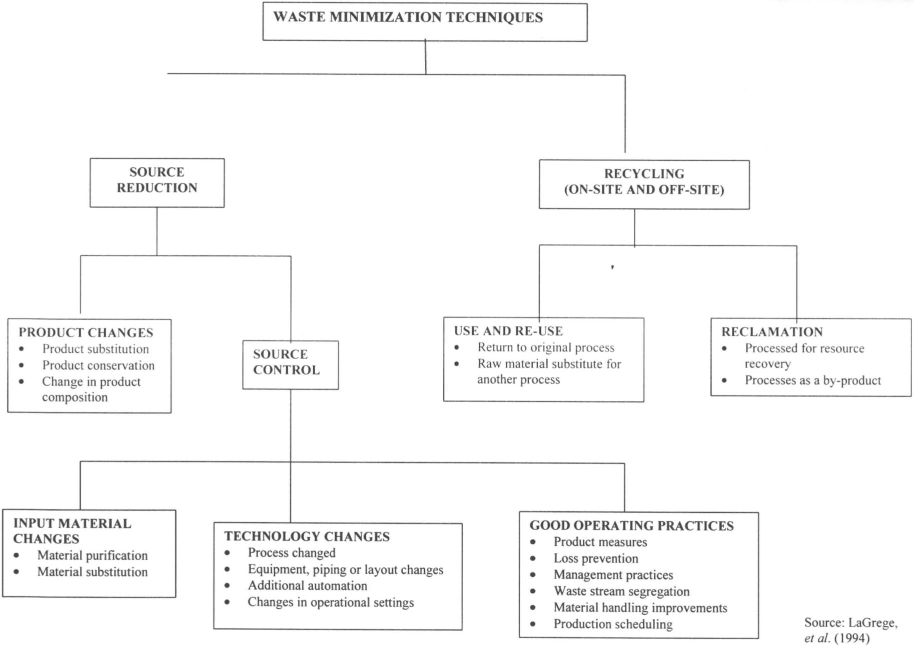
2.4 WASTE MINIMIZATION TECHNIQUES

Waste minimization involves activities, practices of processes undertaken to avoid, eliminate or reduce waste at its source of generation. Various versions of waste minimization techniques have been established since the promulgation of the related environmental regulations (Hirschhorn & Oldenburg, 1989; Higgins, 1989; Hunt and Schecter, 1995; Karen, 1991; Englehardt, 1994; GECF, 1995). An overview of techniques/strategies used in pollution prevention adopted from LaGrega, *et al.* (1994) is illustrated in Figure 2.4.

2.4.1 Source Reduction/Prevention

Prevention from the source is the foremost component in the waste management hierarchy. This can be achieved by good practice (e.g. good operation practice, good engineering and maintenance and good housekeeping), production-process modification (including technology changes, product changes and input material changes) (Englehardt, 1994; Hunt and Schecter, 1995; Beck, 1997).

Early recognition of waste generation aspects during the process and product development stage is extremely important and this constitute an important element towards the concept of clean technologies and clean products (Clift, 1997). This concept covers three complementary purposes : less pollutants discharges, less wastage and less demand on natural resources.



Source: LaGrege, *et al*. (1994)

Figure 2.4 Techniques / Strategies used in pollution prevention

The clean products should

1. Save natural resources

   Waste is not just created when consumers throw items away. Throughout the life cycle of a product – from extraction of raw materials to transportation to processing and manufacturing facilities to manufacture and use – waste is generated. Recycling items or making them with less material decreases waste dramatically. Ultimately, less materials will need to be recycled or sent to landfills or waste combustion facilities.

2. Reduce toxicity of waste

   Selecting non-hazardous or less hazardous items is another important component of source reduction. Using less hazardous alternatives for certain items (e.g., cleaning products and pesticides), sharing products that contains hazardous chemical instead of throwing out leftovers, reading label directions carefully, and using the smallest amount necessary are ways to reduce waste toxicity.

3. Reduce cost

   The benefits of preventing waste go beyond reducing on other forms of waste disposal. Preventing waste also can mean economic savings for communities, businesses, schools and individual consumers.

- **Communities.** Over 4,000 communities in USA have instituted "pay-as-you-throw" programs where citizens pay for each can or bag of thrash they set out for disposal. When these households reduce waste at source, they dispose of less trash and pay lower trash bills.
- **Business.** Industry also has an economic incentive to practice source reduction. When products are manufactured with less packaging materials, they buy less raw material. A decrease in manufacturing costs can mean a larger profit margin, with savings that can be passed on to the customer.
- **Consumers**. Consumers also share in the economic benefits of source reduction. Buying products in bulk, with less packaging, or that are reusable (not single-use) frequently means cost savings.

2.4.2 Recycling

Recycling is the collection and separation of materials arising from waste, and subsequent processing to produce marketable products.

After serving its original purpose, recyclable material has, by definition, some value, such that in its remade form the product has new purpose and its not a waste. Recyclable material made into a similar product to the original is termed primary recycling (Philip, *et al.*, 1999)

There are basic requirements for recycling and these are :

- the collection and the transporting of the waste to be recycled,
- the separation and clean-up of the waste, and
- the processing of the waste to obtain marketable products which have then to be sold.

Whether or not recycling of waste materials is possible within a production process depends on a number of factors (Batstone, *et al.*, 1989) :

1. quantity, quality, uniformity and properties of the waste materials,
2. options for the use or reuse of the waste materials,
3. availability and the price of the virgin or similar materials relative to the cost of recycling and storing the waste,
4. availability of a specific technology to segregate recoverable and valuable materials from the waste (reclamation),
5. assessment (technical, economical and environmental) of the possible impact of the non-recovered waste materials,
6. assessment of long-term risks and liabilities, and
7. logistic constraints.

The benefits from recycling may include (Philips, *et al.*, 1999) :

1. conserving natural resources,
2. saving energy in production and transport,
3. reducing the risk of pollution,
4. saving costs in monitoring,
5. saving costs in treatment and/or disposal, and
6. reducing the demand for waste disposal facilities and landfill space.
7. producing goods more cheaply

2.4.3 Waste Treatment

This is the least preferred option in the waste management hierarchy and only applied when all the other options are exhausted. Various waste treatment technologies are available, ranging from biological treatment, physical-chemical processes, thermal methods to land disposal (Freeman and Harris, 1995). Choices depend upon the waste characteristics, degree of toxicity, treatment objective, economic considerations and regulatory requirements/standards.

2.5 CLEANER PRODUCTION

Most countries focus their attention on end-of-pipe treatment which emphasize on pollution control rather that pollution prevention. Cleaner production gives importance to pollution prevention through waste reduction, recycling or even total elimination (zero-waste concept). It was introduced to reduce the impact of (industrial) hazardous waste on the environment, by both volume reduction and toxicity reduction.

The United Nations Environment Programme (UNEP) has define Cleaner Technology as follows : the continuous application of an integrated preventive environmental strategy to processes and products so as to reduce the risks to human and the environment. To achieve this, life-cycle analysis(or materials audit) needs to be carried out and using waste minimization as a tool (based on waste audit) the objectives of cleaner production could be attained (Agamuthu, 2001).

2.5.1 Benefits

The benefits of cleaner production (or clean technology) are quite similar to the benefits derived from waste minimization, which were described earlier. Briefly, the benefits are as follows (Agamuthu, 2001) :

1. Lower waste management expenses due to
    - (a) reduced on-site handling costs
    - (b) less waste storage area required
    - (c) lower off-site transportation costs
    - (d) less paperwork

2. Savings on reduce costs of raw materials and energy
    - (a) direct use or reuse of a waste in the process
    - (b) recovery of a secondary material and
    - (c) removal of impurities or specific components from a waste to generate a reusable material.

3. Improved productivity – waste minimization usually results in improved production and hence yield improvement.
4. Naturally, cleaner production creates better public images. Also, reduced waste could be translated as healthier working environment for the workers.
5. Liability risks are reduced when the generation, transportation, storage and treatment or disposal of hazardous waste is minimized. This could also mean less impact on the environment.

2.5.2 Implementation

Several approaches are available, and hence the techniques used may vary. Some of the approaches are listed below (Agamuthu, 2001) :

1. Life-cycle analysis and operational changes
    - inventory and trace all raw materials
    - purchase fewer toxic materials, if necessary
    - improve overall operations pertaining to materials purchase, storage and handling
    - maintenance programs established and reviewed regularly
    - proper training for personnel

2. Equipment modifications
    - install equipment that could prevent waste generation or at least reduce the amount of waste
    - redesign to reduce waste generation
    - improve the efficiency of equipment operations
    - equipment should be designed to incorporate recovery or recycling facilities
    - system should not have leaks and spills

3. Production process modifications
    - optimize chemical reactions and raw materials use or reuse
    - substitute non-toxic for toxic substances, especially solvents
    - products should be designed to have minimal or no effect on the environment
    - processes should be optimized to reduce waste generation

4. Recycling and reuse
    - install closed-loop systems
    - recycle on-site or off-site for reuse
    - waste segregation should be practiced, to separate re-materials from non-toxic ones
    - waste exchanges

2.6 WASTE MINIMIZATION PROGRAM IN MALAYSIA

In the Malaysian industry, there isn't any structured waste minimization program promulgated by DOE. The use of cleaner production or waste minimization is still in an infant stage even though industries are generally aware of the benefits accrued from the incorporation of waste minimization practices in manufacturing process. Recycling of wastewater in rubber industry is considered as an example of cleaner production in Malaysia (UNEP, 1994). Perhaps the launching of the Hibiscus Award in 1996 was considered as the beginning point in the effort to promote cleaner technologies and industrial waste minimization program in Malaysia.

The Hibiscus Award is the premier environmental award in Malaysia, given in recognition of companies initiatives and efforts in protecting the environment by incorporating good environmental practices and cleaner technologies. It is organized jointly by Environmental Management and Research Association of Malaysia(ENSEARCH), Malaysiañ International Chamber of Commerce and Industry (MICCI), Business Council for Sustainable Development in Malaysian Manufacturers (FMM), with the support of DOE (NST, 5 Dec. 1997).

According to a report prepared by the Argome National Laboratory and the East-West Center (1994), many incentives exist that encourage investment in pollution control equipment rather than waste minimization technology. For instance, a factory may receive an investment tax credit, an import duty exemption, an accelerated depreciation allowance, or a reduced interest loan for purchasing end-of-pipe environmental control equipment, but the same incentives are not available for purchases of cleaner production equipment.

The Federation of Malaysia Manufacturers (FMM) has expressed an interest developing waste minimization information programs for its members. It has also suggested that the tax law be modified to allow credits for cleaner production/waste minimization technology (Abdul Rani, 1995).

Three important elements of integrated solid waste management hierarchy (source reduction, waste recycling and waste transformation) are not officially and legally incorporated into the Malaysian waste management practice. Organized source reduction and recycling are lacking although a few NGOs do carry out recycling activities (Agamuthu, 2001)

2.7 WASTE MINIMIZATION PROGRAM IN OTHER COUNTRIES

Reflecting both an interest in saving and avoidance of prosecution from stronger environmental regulations, various industries around the world have incorporated waste minimization practices in their operations and production. Many successful examples have been reported from both developed and developing countries (Freeman, *et al.*, 1992; Critenden and Kolaczkowski, 1995; Shen, 1995).

Development of waste minimization in UK, North America and European Union have achieved significant milestone (Philips, *et* al., 1999). In US, waste minimization has its origins in the Resource Recovery and Reauthorization Act (RCRA), since 1976. in addition to traditional legislative mechanisms, the EPA has built co-operative partnerships with businesses, citizen groups, state and local governments, universities and trade associations. Among the collaborative efforts are 35/50, Waste Wi$e, Green Lights, Energy Star, WAVE, Design for the Environment and Project XL (Eighmy & Kosson, 1996).

The introduction of integrated pollution control (IPC) into UK legislative mechanisms has led to the adoption of waste minimization initiatives across all prescribed processes and many other processes. Aire and Calder Project in Yorkshire and Project Catalyst are among the successful projects which reduced the demand of water by 1.9 million meter^3 per year and a potential saving of 1.8 million tonne of liquid effluent (Johnston, 1994; Atkins, 1994; UNEP, 1994).

Japan is considered as a technologically-advanced country in Asia. Japan can probably be considered the world's premiere recycling country. This is due to

(i) its limited space and resources
(ii) its enormous reliance on imported primary raw materials (including 98.8% of its oil and 99% of its iron ore)
(iii) the need to control pollutants from various industrial activities
(iv) government support

These factors influenced the waste management policies in Japan and has resulted in the implementation of many creative and sophisticated techniques (Englande, 1994).

In Taiwan, a developing nation, a national Industry Waste Minimization (IWM) master plan was approved in July 1990, which called for an aggressive program to demonstrate IWM techniques and to provide technical assistance and consultation to the industry. The total estimated benefit accrued from this program was over US$70 million from 1991 to 1994 (Chang, *et al.*, 2002).

2.8 SOLIDIFICATION/STABILIZATION TECHNOLOGIES

Solidification / Stabilization (S/S) is a term often used to designate a technology employing additive(s) to reduce the mobility of pollutants, thereby making the waste acceptable under current land disposal requirements (Li, *et al.*, 2001). It is a technique that encapsulates the waste in a monolithic solid of high structural integrity. S/S technologies have been widely applied in waste treatment for a wide variety of hazardous waste materials, such as spent pickle liquor, industrial sludges, filtered cakes, contaminated ashes and soils. It is also effective in immobilizing many low-level radioactive wastes (Freeman and Harris, 1995). Solidification does not necessarily involve chemical interaction between the waste and solidifying reagents, but may mechanically bind the waste into the monolith. Contaminant migration is restricted by vastly decreasing the surface area exposed to leaching and/or by isolating the wastes within a relatively impervious capsule (Bishop, 1995).

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S/S technology is a viable technical option which has historically proven to be cost effective and it has been specified by EPA as Best Demonstrated Available Technologies (BDAT) for a number of waste streams and some can be used as a basis for "delisting" a waste as hazardous under RCRA (Bishop, 1995; Means, *et al.*, 1995; USEPA Engineering Bulletin, 1997).

Although the terms stabilization and solidification are often used interchangeably, they represent different concepts in waste treatment. Stabilization processes attempt to reduce the solubility or chemical reactivity of a waste by changing its chemical state or by physical treatment. The hazard potential of the waste is reduced by converting the contaminants to their least soluble, mobile or toxic form.

Stabilization/solidification (S/S) technology refers to treatment process that are designed to

i) improve the handling and physical characteristics of the waste,

ii) decrease the surface area of the waste mass across which transfer or loss of contaminants can occur, and

iii) limit the solubility of any hazardous constituents of the waste such as by pH adjustment or sorption phenomena.

The most important factor whether a particular S/S process is effective in treating a given waste is the reduction in the short-term and long-term leachability of the waste. Leaching can be defined as the process by which a component of waste is removed mechanically or chemically into a solution from the solidified matrix by the passage of a solvent such as water. Resistance to leaching will depend on both the characteristics of the solidified/stabilized waste and on those of the leaching medium it will come into contact with (Bishop, 1995).

S/S process employs systems which both solidify the waste mass and eliminate free liquids , and stabilizes the contaminant in their least soluble form. The overall objective is to minimize the rate of leaching pollutants from the resulting waste form. These process typically involves the addition of binders and other chemical reagents to the contaminated sludge to physically solidify the waste and chemically bind the contaminants into the monolith (Bishop, 1995).

Binder systems can be placed into two broad categories, inorganic or organic. Most inorganic binder systems in use include varying combinations of hydraulic cements, lime, fly ash, pozzolans, gypsum and silicates. Organic binders used or experimented with include epoxy, polyesters, asphalt/bitumen, polyolefins (primarily polyethelene and polybutadiene) and urea formaldehyde. Combinations of inorganic and organic binder systems have also been used. These include diatomaceous earth with cement and polystyrene, polyurethane and cement, polymer gels with silicates and lime cement with organic modified clays (Bishop, 1995).

Commercial vendors have typically developed generic processes into proprietary processes by adding special additives to provide better control of the S/S process or to enhance special chemical or physical properties of the treated waste in order to ensure environmentally safe ultimate disposal of problematic industrial wastes (Pojasek, 1979;

Zamorani, 1994; Freeman & Harris, 1995; USEPA/ORIA, 1996). Table 2.5 summarizes some of the commercially available proprietary S/S technologies.

Table 2.5
Summary of some commercially available proprietary S/S processes.

Proprietary S/S Process	Description
CALCILOX®[1]	• Particular wastes obtained in the mining, preparation and coal combustion (e.g. coal fines and flue gas sesulfurization (FGD) are treated with an additive named "Calcilox". • Calcilox additive is a dry, free-flowing,light grey coloured powder of inorganic nature and it's hydraulically active.
CHEMFIX®[1]	• Based on the reaction between the soluble silicates and silicate setting agents that react in a controlled manner to produce a solid matrix. • A cross-linked, 3-dimensional polymer matrix is formed which is similar to natural pyroxene minerals-high stability, high melting point, a rigid and friable structure.
TERRA-CRETE®[1]	• A unique waste-to-waste approach for the treatment of FGD sludges. • Utilizes 2 similar compound with cementitious properties that are obtained from the FGD sludge itself – gypsum ($CaSO_4$) and calcium sulfite ($CaSO_3$).
TERRA-TITE®[1]	• Utilizes cementitious additives. • The product exhibits low permeability, high strength and insignificant leachability. • Specially designed to treat waste containing Hg, Cr, Ar and organic wastes.
SEALOSAFE®[1]	• Utilizes calcium containing cement and aluminate and/or alumino silicate to mix with waste dissolved in water to produce a product, called STABLEX. • It exhibited superior properties in terms of low leachability, low permeability and high strength.
Separation and Recovery System / Ecology of France (SRS/EIF) Process[2]	• Utilizes lime-based process to permanently fix waste in a matrix product. • Particularly good for testing waste with high organic content, e.g. refinery intermediates of final products, halogenated chemicals, PCBs, pesticides, painting waste and acid sludges.
Sulfur Polymer Encapsulation (SPE)[3]	• A thermoplastic material • It has relatively low melting point (120°C) and melt viscosity (about 25 centipoise) and thus can be processed easily by a simple heated stirred mixer. • Higher compressive and tensile strength
Pheonix Ash Technology (PAT) [3]	• Involves the conversion of a mixture of fly ash, volcanic ashy or kiln dust into a solid form, typically brick. • Relies on mechanical compression during the initial onset of hydration, and uses lower moisture levels than cementitious slurry. • Applicable to wide variety of materials, particularly viable for fine inorganic materials.

Sources: 1. Pojasek, 1979; Zamorani, 1994; 2. De Franco, 1990; 3. EPA/ORIA, 1996.

The specific technology used is based on several factors including the treatment objectives, waste characteristics (both chemical and physical), regulatory requirements, performance requirements, economics, resulting volume, logistic constraints and material availability. In addition , site specific factors such as location, climate and hydrogeology must also be taken into consideration to assure an acceptable performance (Wiles, 1989 and Wiles & Barth, 1992).

2.8.1 Grout/Cement Based Techniques

Cement-based stabilization/solidification is one of the most prevalently used techniques because of the relatively simple and inexpensive nature, compatibility with wide variety of disposal scenarios and ability to meet stringent processing and performance requirements. This technique is also commonly called grouting and the mixtures so obtained grouts (USEPA/ORIA 1996).

Cementitious materials include cement, ground granulated blast furnace slag, fly ash, lime, cement kiln dust and silica fume. Various combinations of the cementitious material and other proprietary additives are mixed with wastes to improve waste-form performance, such as enhancing the immobilization of contaminants, increase the compressive strength, eliminate free liquids and reduce the resulting volume increase (Bishop, 1995).

Among these, Ordinary Portland Cement (OPC) is the most commonly used binding agent. The waste material 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 bonding the cement. The waste are incorporated into the cement matrix and, in some cases, undergo physical-chemical changes that further reduce their mobility in the waste-cement matrix. Small amounts of fly ash, sodium silicate, bentonite, or proprietary additives are often added to the cement to enhance processing (USEPA, Engineering Bulletin, 1992).

2.8.2 Inorganic waste

Generally cement-based S/S is suitable as a treatment alternative for materials containing inorganic, semi-volatiles and/or non-volatiles organics. The effectiveness of cement-based system to immobilize heavy metal wastes, as well as soils and sludges contaminated with heavy metals, has been repeatedly demonstrated, in both laboratory experiments and cleaning contaminated sites (Freeman and Harris, 1995).

Sively, *et al.* (1986) and Conner (1990) indicate that most cement-based waste forms are initially at pH 10-11, as a result, the metals are retained in the form of insoluble hydroxide or carbonate salts within the hardened structure. In another words, the naturally high pH values are usually desirable for heavy metal (e.g. As, Cr, Ni, Cu, Zn) immobilization because most metal hydroxides have minimum solubility in the pH range of 7.5-11. Some metals, for example lead, is amphoteric-shows solubility at both low and high pH, but on the other hand, insoluble at pH 7 to 11 (Shively, *et al.*, 1986; Conner, 1990; Bishop, 1995).

2.8.3 Organic Waste

The opportunities to capture and immobilize organic materials in cement-based solidification process are limited (Jones, *et al.*, 1992). Due to the hydrophobic nature of many organic waste materials and the surface tension, organic compounds (e.g. oil, grease, trichloroethylene, phenol, etc) tend to retard cementitious reactions, inhibiting the formation of solid monolith mass and easily leached from the waste forms (Freeman and Harris, 1995; Bishop, 1995). As a result, it reduced the final strength and is not easily stabilized. They may also reduce the crystalline structure formation resulting in a more amorphorous material.

Organics, even in small amounts, can interfere in the performance of S/S processes. However, at what concentration the organics will interfere with the cementitious reaction is still questionable (Vipulanandan and Krishnan, 1990). Conner (1990) reported that cement-based S/S works satisfactory for liquid and sludge wastes with up to 15% (by volume) of organic constituent.

Research has been conducted into the use of various additives (e.g. organically modified and natural clays, vermiculite and soluble sodium silicates) in order to reduce the organic contaminants' interference with cement hydration and enhance stabilization

(Brown, *et al.*, 1992); Lo, *et al.*, 1997). Investigations have indicated that true bonding occurs between organically modified clays and phenol (Soundarajan, 1992).

Clay materials, such as bentonite, with high cation-exchange capacity and extensive specific surface, are often used to extend the range of waste suitable for fixation to inorganic waste containing up to 5% of organics. Vermiculite and montmorillonite clays which have cation-exchange capacities in the range of 130 to 150 meq per 100g also demonstrate their adsorptive capacities for organic compound (Batstone, *et al.*, 1989).

For solidification of mixed waste, extensive research has been carried out over the years, including the use of activated carbon, exchanged clays (Pollard, *et al.*, 1991) and zeolite (Cullinane and Jones, 1992; Cioffi, *et al.*, 1996). The advantages and disadvantages of cementitious S/S processes are presented in Table 2.6.

2.8.4 Evaluating Performance of S/S

A wide range of performance tests may be used in conjunction with S/S treatability studies to evaluate short and long term stability of the treated waste. These include total waste analysis for organics, leachability studies using various methods, permeability, unconfined compressive strength (UCS), treated waste and/or leachate toxicity endpoints and durability test (freeze/thaw and wet/dry weathering cycle tests) (LaGrega, *et al.*, 1994; Means, *et al.*, 1995; Freeman and Harris, 1995).

Table 2.6
Summary of advantages and disadvantages of cementitious S/S processes

	Advantages	Disadvantages
1.	Low capital investment of equipment and operating costs.	Large amount of raw materials are required
2.	Materials needed are relatively cheap and easily obtainable.	Weight and volume increase of treated product, hence increased transportation and disposal costs
3.	Techniques for processing are relatively well established and compatible to a wide variety of disposal scenarios	Incompatible with certain types of waste, particularly those containing organic compounds, that may retards setting
4.	Natural alkalinity of cement helps to neutralize acidic waste	Treated waste are relatively vulnerable to leaching, especially mild acids, additional sealant may be required
5.	Extensive dewatering of wet sludges or waste is not necessary as water is required for hydration	Mechanism of stabilization not well established
6.	Physical properties of treated waste can be varied from soft clay to a monolithic material by selectively varying the ratio of binding agent	

Sources : Batstone, *et al.*, 1989; LaGrega, *et al.*, 1994.

2.8.4.1 Leaching test

Leaching tests are normally used to evaluate the performance of solidified/stabilized waste. Leaching tests are used to estimate the potential for the stabilized waste form to release contaminants to the environment. In general, laboratory leaching tests are designed either to simulate a field leaching scenario or to measure a specific fundamental leaching property of the material being tested (Glasser, 1997).

However, in view of the variety of possible landfill scenarios, no single leach testing procedure or protocol can duplicate all possible field conditions. Ideally, the treated waste would be leach-tested with surface, ground or rainwater that is present at that site. As alternatives, water, aqueous solutions of acids and salts, or organic liquids to model various disposal scenarios may be used in leaching tests, to determine waste composition, measure diffusion coefficients, or for other specific test purposes.

Studies have demonstrated that a great number of test factors or variables affect the leachability characteristics of solidified/stabilized products. The major factors include surface area of the waste, alkalinity of the solidified/stabilized product, physical nature of the waste (monolithic, crushed or pulverized), type of liquid-solid contact (static, dynamic or in flow), type of leachant(distilled water, acetic acid or simulated acid rain), extent of mixing/agitation, leachant-to-waste ratio, waste and leachant contact time, number of elutions used, extraction vessel, temperature and pH adjustment (Conner, 1990; Albino, *et al.*, 1996). Generally, these leaching tests can be categorized as extraction test and leach test (Sharma and Lewis, 1994).

(a) **Extraction test** (e.g. Toxicity Characteristics Leaching Procedures (TCLP), Extraction Procedure (EP) Toxicity Test), are batch procedures and generally involve agitation of ground or pulverized wastes (particle size 9.5 mm) in a leachant to achieve continuous mixing, for a specified period of time. The leachant may be acidic or neutral, in most cases is diluted acid. Extraction normally last from hours to days and are therefore short term test. It should be noted that most of the extraction test use a leachant-to-waste ratio of 20:1, so that the maximum concentration of contaminants that can be attained in the leachate is 5% of that in the original solid (Sharma and Lewis, 1994).

Studies have shown that the final pH of the leachate is one of the prime controlling factors in metal leaching. With the larger surface area exposed to the leachant, the extraction test are designed to simulate the leaching potential of a contaminant in a "mismanagement" leaching scenario, where it is disposed in a landfill designed for municipal refuse. Such landfills are known to generate organic acids during decomposition of organic matter in the refuse and the use of acetic acid in the leachant is to simulate those acids (Blackburn, et al., 1988; Conner, 1990; Reynolds, 1991).

The TCLP test has been commonly used by US EPA and state agencies to evaluate the leaching potential of S/S treated waste. It is a second generation extraction procedure which improves upon the existing EP technique and allows for the inclusion of an expanded list of volatile and semi-volatile organic compounds. It should be highlighted that the same test is also being used in Bukit Nanas Integrated Hazardous Waste Management Center, Malaysia.

(b) **Leach testing** involves no agitation of monolithic waste mass. Leach tests may be run under two conditions : (i) static condition – the leachant is not replaced by a fresh solution, assuming leaching takes place under static hydraulic conditions, or (ii) semi-designated intervals [e.g. American Nuclear Society Leach Test (ANSI/ANS 16.1)], assuming leaching takes place under non-equilibrium conditions under well managed landfill sites (Sora, *et al.*, 2002).

The ANSI/ANS 16.1 is intended mainly to develop a figure-of-merit (Leachability Index) for comparing the leaching resistance of S/S treated waste and also to indicate contaminant release rate. This leaching protocol assumes that internal bulk diffusion from a semi-infinite medium is the most likely rate-determining mechanism during the initial phases of the leaching process, and concentration of the species leached is zero at the surface of the waste form after leaching commences.

2.8.4.2 Compressive Strength

For stabilized cement-like waste, the compressive strength test can provide several pieces of useful information, including the following :

- The ability of the stabilized waste to with-stand overburden loads,
- The optimum water/additives ratios and curing time for cement setting reactions, and
- The improvement in strength characteristics from the unstabilized to the stabilized waste.

In addition, the test result would be expected to correlate with the effectiveness of stabilization of inorganic waste as the inorganic constituents are tied in the hydrating matrix (Grube, 1992; LaGrega, *et al.*, 1994). Current US EPA regulation requires that the stabilized/solidified products have a minimum of 28 days unconfined compressive strength (UCS) of 50 psi.