CHAPTER 1

INTRODUCTION

1.1 GENERAL

One of the serious problems of the technological era is the steadily increasing amount of toxic and hazardous wastes being produced daily by industry, agricultural activities, hospital and research laboratory. Sludge or 'biosolids' as it is now called is a waste product of certain industries. Huge amounts of sludge are produced and must be disposed of. Sludge can contain heavy metals and toxic chemicals that are difficult to dispose of properly. Incineration, landfilling and ocean dumping, all have major flaws and are strictly regulated by the federal government. Perhaps the most efficient way to dispose of sludge is to spread it lightly over land, as plants thrive on sludge. This may help the plants, but the heavy metals and toxic chemicals can also contaminate groundwater and disease causing bacteria can spread to humans or other animals (Rhyner *et al.*, 1995).

In order to protect human health and the natural environment, it is imperative that safe handling and disposal techniques for these wastes be used. The Department of Environment (DOE) Malaysia has launched a strict vigilance on the disposal of toxic and hazardous wastes and has been encouraging its proper treatment and disposal. The DOE also intends to introduce regulations to control the disposal of toxic and hazardous wastes and will be adopting "cradle-to-grave" tracking procedure for following the waste from the generator to its ultimate disposal site.

The term hazardous waste has been defined by Resource and Conservation Act (RCRA) legislation of The United States as "a solid waste, or combination of solid waste because of its quantity, concentration on physical/ chemical/ infections may cause an increase in mortality or an increase in serious irreversible or incapacitating reversible illness or pose a substantial present or potential hazard to human health or environment when improperly treated, stored, transported, or disposed of or otherwise managed".

United States Environmental Protection Agency (USEPA, 1990) identifies a waste as hazardous if it can cause or contribute to an increase in mortality or can pose a substantial threat to human health or the environment when improperly managed. Malaysia's own Environmental Quality (scheduled waste) Regulations, 1989 gives a definition of 'incompatible scheduled waste' to mean scheduled waste specified in the Fourth Schedule, when mixed will produced hazardous situation through heat generation, fires, explosions or release of toxic substances.

A series of survey to determine the types and quantities of toxic and hazardous wastes has been conducted (Mackenzie & Davis, 1991). There are many different approaches to the treatment and disposal of hazardous wastes, just as there are many different types of the wastes. Many types of industry are small to medium scale industries that could not afford expensive treatment facility and technical support of skilled personnel. The lack of suitable landfill burial sites further aggravates the problem of disposal of toxic residues (Holmes *et al.*, 1993).

1.2 A BRIEF INTRODUCTION OF PALM OIL INDUSTRY

The oil palm, *Elneis guineensis* which originated from West Africa was introduce to Malaysia in 1870 as an ornamental plant. Its use as a crop was not developed until 1917, when it was grown commercially. The modern expansion of the industry can be traced back to the 1960s when the Malaysian Government on a massive programme of agricultural diversification. Today, oil palm is the leading agricultural crop in Malaysia, covering about 2 million hectares or third of the total cultivated area. The refining of crude palm oil commenced in the early 70s in response to the Government's call for increased industrialization. The emergence of refineries marked the introduction of a wide range of processed palm oil products. In 1995, Malaysia remained as the world's largest producer of palm oil with 7.8 million tones or 51 % of world production. Palm oil is expected to contribute about 25 % of the forecasted 105 million tonnes of oils and fat demand by the year 2005. In terms of export, Malaysia remained as the largest palm oil exporter with 6.5 million tones, capturing a share of 62 % of world total palm oil exports.

1.3 THE PROCESSING OF PALM OIL

Figure 1.1 shows a schematic flow diagram of a palm oil mill process. Palm oil is extracted from the pericarp of the fruits of the oil palm. The process involves a number of stages. The harvested bunches of oil palm fruits are steam sterilized. The sterilization of the fresh fruit bunches (FFB) is to inactivate the enzymes responsible for the breakdown of oil into free fatty acids and to loosen the fruits from bunches. The condensed steam with entrained debris together with some oil from the fruits is known as the sterilizer condensate. Individual fruits are stripped from bunches in a rotary-drum thresher. The fruits are then fed to the digester while the empty fruit bunches are disposed of either by incineration to obtain ash rich in potassium which is used as a fertilizer or put to a variety of uses including mulching in sandy soil.

During digestion, the fruits are reduced to a near homogenous mass by beating against baffles and vigorous stirring in a steam-jacketed kettle. After digestion, the fruit mass passes into a screw press. The oil flows from the fruit through a perforated cage surrounding the screw. The deoiled fibre-and-nut mixture is continuously expelled through a cone at the end of the press. The crude oil expelled from the press contains oil, water and solids. The mixture is then clarified to separate the oil from the other constituents. This is done by first a static settling of the mixture in tanks. The oil is the decanted off and passed through a centrifugal purifier and a vacuum drier to remove solids and moisture. The clarified oil is stored while the heavy dark sludge known as palm oil sludge is further centrifuged to remove some of the residual oil and is then discarded. This forms the bulk of the effluent discharged during palm oil extraction. Waste liquors are also produced at other stages from spillage, steam traps and processes used to recover kernels from nuts.

For every 100 tonnes of FFB processed only 22 tonnes are removed as palm oil, the main economic product. The remaining 78 tonnes are removed as both liquid and solid wastes. A large volume of liquid waste is produced during the extraction process. This liquid waste normally consists of sterilizer condensate, clarifier sludge and hydrocyclone washings. In the present study, the clarifier sludge was used and is referred to POME. Of the solid wastes, the fibre and shells are often used as low grade boiler fuel. The empty fruit bunches produces a sooty smoke which pollutes the atmosphere.

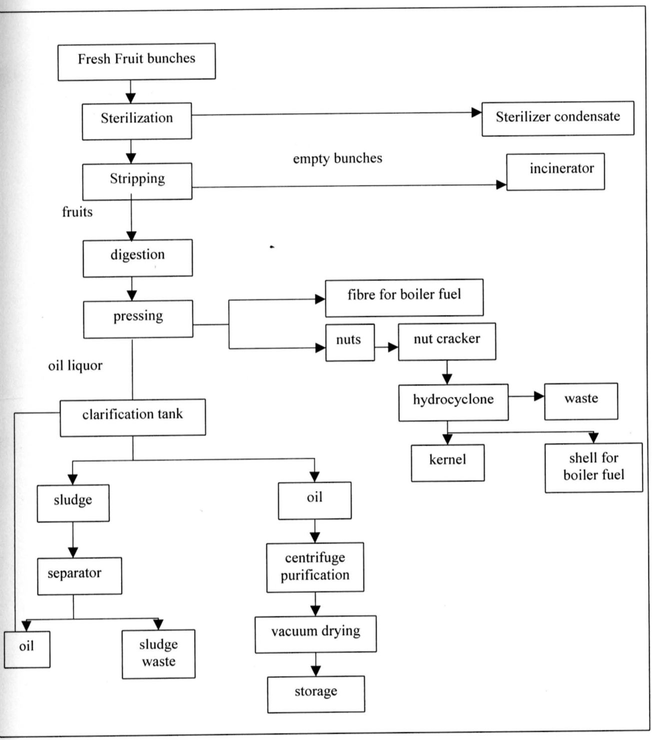

Figure 1.1 Schematic flow diagram of a palm oil process

1.4 PALM OIL AND ENVIRONMENT

The palm oil development in Malaysia has been colorful. Starting off as ornamental, the crop has developed to the multi billion ringgit industry as is witnessed today. Success in the plantation development carried the crop to a new challenge; that is the processing technology. Almost single handedly, we developed technologies that are not only economically sound but also sensitive to environmental needs. Throughout its entire development in Malaysia, both upstream and downstream, the palm oil and its products have always been linked with the environment. Such a rapid income in both upstream and downstream activities would have resulted in uncontrollable environmental pollution.

Palm sludge is mainly organic in nature and highly degradable. Therefore it is practically non-toxic, which is not according to traditional definition of hazardous defined by Resource and Conservation Act (RCRA). According to RCRA, the waste is listed as hazardous because it exhibits one of the characteristics of hazardous wastes which is ignitability, corrosivity, reactivity and toxicity. In view of its particularly high BOD and COD, POME sludge is especially polluting. Thus its detrimental effects on aquatic life are well known. Its direct discharge into receiving streams and rivers poses a serious treat to the environment and quality of life in rural areas. It also produces a strong odour when left in open space (26 – 29^0 C) for a few days. In the early seventies, the majority of the palm oil mills had discharged POME directly into waterways without prior treatment. All forms of aquatic life, both flora and fauna in these waters died due to the depletion of oxygen. Following a nationwide survey, of the 49 rivers in Peninsular Malaysia, 42 were grossly polluted and biologically "dead" due to direct discharge of POME into the rivers. In some cases, it even led to the production of obnoxious odours. This pollution had affected the livelihood of fishermen living along many rivers in Malaysia (Tan, 1985).

Consequently, the Department of Environment (DOE), Ministry of Science, Technology and Environment, Malaysia has stipulated stringent standards in order to protect and manage the environment (see Table 1.1). With the result, The Environmental Quality (Prescribed Premises) (Crude Palm Oil Order, 1977) came into force on July 1978. DOE also exercises control through the issue of a licensed which has these effluent standards as the principal conditions attached. Based on the amount of BOD discharged, a levy of effluent related fees is imposed. Biological oxygen demand (BOD) was the key parameter in the standard. From the initial BOD of 25 000 ppm of untreated POME, the load was reduced to 5 000 ppm in the first generation, down to the present BOD of 100 ppm.

With strict adherence to these regulations POME pollution nightmare has become a thing of the past. In 2000, the population equivalent of the POME pollution load was reduced from 15.9 million people 2 years earlier to only 2.6 million people. With further improvement on treatment technology, the BOD load decreased dramatically in 1999 to less than 1.6 million people though the crude palm oil (CPO) production was well above 6 million tonnes. POME either in raw or treated forms, contains a high level of plant nutrients. When the BOD level is brought down to below 5000 ppm, the digested POME is allowed for land application.

Table 1.1 POME Discharge Standards

Parameter	Std. A 1/7/78	Std. B 1/7/79	Std. C 1/7/80	Std. D 1/7/81	Std. F 1/7/82	Std. F 1/7/84
pH	5 – 9	5 – 9	5 – 9	5 – 9	5 – 9	5 – 9
BOD	5 000	2 000	1 000	500	250	100
COD	10 000	4 000	2 000	1 000	-	-
TS	4 000	2 500	2 000	1 500	-	-
SS	1 200	800	600	400	400	400
AN	25	15	15	10	150 (a)	100 (a)
ON	200	100	75	50	-	-
TN	-	-	-	-	300 (a)	200 (a)
O&G	150	100	75	50	50	50

(a) – value of filtered sample

1.5 STABILIZATION AND SOLIDIFICATION (S/S)

The terms "stabilization and solidification" refers to treatment processes that are designed to accomplish one or more ways to improve the handling and physical characteristics of the waste as in the sorption of free liquids, decrease the surface area of the waste mass across which transfer or loss of contaminants can occur and limit the solubility of any hazardous constituents of the waste, e.g., by pH adjustment or sorption phenomenon (USEPA, 1982). The preliminary benefit of stabilization techniques is that they limit the solubility or mobility of the contaminants with or without changing or improving the physical characteristics of the waste. Stabilization usually involves adding materials that will ensure the hazardous constituents are maintained in their least mobile or toxic form. The additions of lime or sulfide to a metal hydroxide waste to precipitate the metal ions or the additions of absorbent to an organic waste are examples of stabilization techniques (Tseng & Ho, 1987).

Stabilization/ solidification is a proven technology for the treatment of hazardous wastes and hazardous waste sites. Technical reasons for the selection of stabilization/solidification as a remediation technology include (Rhyner *et al.*, 1995);

- Improves the handling and physical characteristics of the waste; e.g., sludge are processed into solids.
- Reduces transfer or loss of contained pollutants by decreasing the surface area
- Reduces pollutant solubility in the treated waste, generally by chemical changes
- Techniques for processing sludges are well established, however they are not set for soils and debris
- Residues from the treatment of hazardous wastes by physical/chemical/biological or incineration technologies can be further treated by stabilization and solidification process.
- Because of excavation problems, in-situ treatment by stabilization and solidification is the only viable management technique in many cases.
- Alternate hazardous waste treatment and disposal techniques are often economically prohibitive.

1.6 PURE MODEL STUDY

Pure model study on the effect of inorganic constituents has been carried out in the past (Cartledge *et al.*, 1994). These studies have demonstrated that the early hydration reactions of cement were modified by the incorporation of heavy metals. This has an important implication on the mechanism of immobilization of heavy metals by cement-based stabilization and solidification. Studies on the effect of heavy metal oxides (Cr, Cu, Zn, As, Cd, Hg and Pb) on the physical properties of cement indicated that the metals influence the hydration and microstructure of the hydrated cement in the early stages of hardening, thus affecting strength development (Alloway & Ayres, 1994).

The retardation of cement hydration was thought to be due to the formation of colloidal membrane coating around the hydrating cement grains by precipitation of the mixed basic lead salts. Cartledge, *et al*, (1990) investigated the behaviour of Cd and Pb salts towards cement-based solidification using TCLP leaching test, conduction calorimetry and solid state NMR. The study revealed that in cement solidification of aqueous sludge produced by lime treatment of solutions containing Cd^{2+} and Pb^{2+}, the concentration of cadmium was very low whilst that of lead was considerably higher. The Cd/cement system involves early formation of $Cd(OH)_2$.

In the case of waste sludge this occurs before cement was added while in the case of soluble Cd salts immediately after cement was added. This provides a nucleation site for precipitation of C-S-H gel and $Ca(OH)_2$. Consequently Cd occurs in the form of insoluble hydroxide with a very impervious coating.The immobilization of Zn and Cd were found to be mainly via precipitation, sorption and chemisorption. Hg on the other hand is immobilized by physical encapsulation. Porosity is generally increased by the addition of $Pb(NO_3)_2$. A study on the interfering effect of Cu, Pb and Zn showed that these elements have detrimental effect on the physical properties of the stabilization and solidification sludge (Clair *et al.*, 1994).