

## CHAPTER 4

### MATERIALS AND METHODS

#### 4.1 OBJECTIVES

The experiment attempts to study the aspects of compressive strength and leaching of heavy metals from stabilized POME sludge and simulated metals. Stabilizing hazardous wastes will reduce leachability and increase bearing strength of the hazardous wastes before landfilling or storage in other special depositories, where they will be attacked by ground water and acidic rain. The fluid leached through the waste is known as leachate. This experiment attempts to simulate the behaviour under actual conditions of the stabilized waste when disposed off in the landfill. Cement replacement materials such as pulverized fly ash (PFA) is cheaper than ordinary portland cement (OPC), but have almost similar physical properties and chemical contents. Substitution of cement by PFA is according to certain fixed percentages into various C/S<sub>d</sub> (cement to dry sludge) ratios to determine the best condition available.

##### 4.1.1 Leaching Test

The objective of this test is to compare leaching from different S/S waste with various C/S<sub>d</sub> ratios and to assess the effectiveness of the cementitious additive in increasing retention of heavy metals. Leaching is defined as the process by which a component of waste is removed mechanically or chemically into solution from a solidified matrix by the passage of a solvent or extractant (water or acetic acid). The purpose is primarily to compare leaching from the different stabilized system and to access the effectiveness of the cementitious additives of the hazardous metals. This process determined the optimum amount of stabilization additive to use for maximum metal removal.

Leaching test evaluates the maximum concentration of contaminants that leachant or extractant can remove from the hardened waste. The contaminant concentration level is analysed and evaluated against the toxicity circumstances, heavy metals will probably leach more from the solidified wastes. Laboratory testing of stabilized waste leachability was aimed at simulating expected field conditions as closely as possible. In this respect, it is useful to consider two disposal scenarios for solidified wastes. In the well-managed disposal scenario, the solidified wastes are buried below the level of ground water table. The waste is therefore expected to keep its physical integrity. The leaching medium is ground water or infiltrated rain water well buffered by the interaction with the overlying soil, the flow rate of leaching medium is low.

In the laboratory test, deionised water with pH of 6.7 is used as the leaching medium. In the mismanaged disposal scenario, the solidified wastes are subjected to weathering. The leaching medium could be acidic water from atmosphere or microbial degradation sources. 0.5 M HAc (pH 2.89) was used to simulate acidic rain. The experiment was also concerned about simulation of leaching of solidified wastes if they were to break down after a period of time or as a result of other consequences. The surface area of contact between solidified wastes and leaching medium will increase and the test was based on the fact that under these circumstances, heavy metals will probably leach more from the solidified wastes.

#### **4.1.2 Compressive Strength Test**

The test was carried out to obtain the strength development of stabilized/solidified samples for different periods of curing age. In S/S process, one of the aims is to obtain an adequate strength development of treated wastes in order to improve structural integrity and to limit solubility. Strength test values indicate how well the materials will hold up under mechanical stresses created by overburden and earth-moving equipment.

Strength of cement paste is commonly considered to be its most valuable property and strength usually give an overall picture of the quality of concrete because it is directly related to the structure of cement paste.

Stabilization and solidification of hazardous wastes sludge into non-hazardous wastes and conversion to commercially valuable materials such as construction materials can easily be handled and transported for landfilling. The strength test for stabilized wastes showed a preliminary qualification for serious consideration as construction materials. Cement replacement material such as PFA is added to decrease the use of ordinary portland cement and to obtain a higher strength result.

## **4.2 PROGRAM SCHEDULE**

The proposed experimental program was suggested as an alternative treatment of palm oil mill effluent sludge by the process of stabilization and solidification with ordinary portland cement and cement replacement material and also the study of simulated metals for pure model study.

### **4.2.1 Preliminary Work**

The design of experiments, preparation of materials and equipment, determination of sludge characteristic and trial mix were carried out at the initial stage of the program.

### **4.2.2 Laboratory Studies**

The experiments work including casting, curing, leaching test, UCS test were carried out after the required materials and equipment are available. Appendices A and B show the casting date and curing age of solidified samples for UCS and TCLP tests.

### **4.2.3 Data Analyses**

Interpretation of data could only be carried out after sufficient chemical analyses were performed.

### **4.2.4 Report Writing**

This report was written in stages as the experiments progressed.

## **4.3 PRELIMINARY WORK AND PREPARATION OF MATERIALS**

Some preliminary studies have to be done before the actual experiments can be done. The materials and equipment required by the experiments were prepared before the actual laboratory work started. The main materials used are ordinary portland cement (OPC), pulverized fly ash (PFA), palm oil mill effluent (POME) sludge and chemicals such as zinc, iron and copper for pure model study. POME sludge was obtained from Kilang Kelapa Sawit Elmina Sdn. Bhd., Sungai Buloh, Selangor.

The instruments such as TCLP extractor bottles, beakers and containers that were used in these experiments have to be soaked in a decond 90 to remove organic compound and then 5 % nitric acid to remove any bounded metals and finally soaked in distilled water for 24 hours. These steps are to prevent any presence of impurities during the leachability analysis, which can reduce the accuracy of the test.

### **4.3.1 Sludge Moisture Content**

This step was preliminary prior to preparation of solidified wastes. The moisture content of the sludge is the ratio of the mass of a dry sludge and the origin raw sludge. The percentage of moisture content of raw sludge is needed in the determination of the quantities of sludge and cement required for each C/S<sub>d</sub> ratios. Methods and procedures were based on 'Standard Methods for the Examination Water and Wastewater'

(Greenberg *et al.*, 1992) and are summarized in section 4.5 The results of the sludge moisture content are shown in Appendix C.

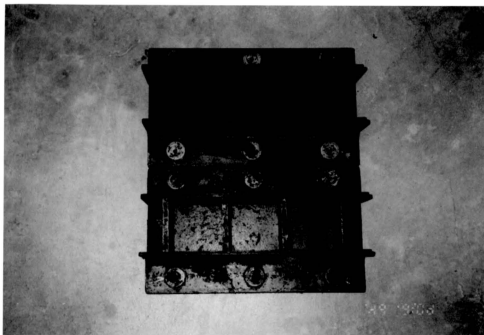
#### **4.3.2 Sludge Specific Gravity**

The specific gravity (SG) of a substance is the ratio of the density of the substance,  $p$  to the density of a reference substance  $p'$  at a specific condition. The reference most commonly used for solids and liquids is  $H_2O$  at  $4\text{ }^\circ\text{C}$  that has the density of  $1000\text{ kg/m}^3$ . The method to determine the sludge specific gravity was based on section 271  $^\circ\text{F}$  of Standard Methods for Examination of Water and Wastewater. The results of sludge specific gravity are shown in Appendix D.

#### **4.3.3 Preparation of Moulds**

In order to provide sufficient samples for the UCS test, 6 cubic moulds with size  $50\text{ mm} \times 50\text{ mm} \times 50\text{ mm}$  were designed and made from steel. At the same time, one litre high density polyethylene (HDPE) plastic container were prepared as a mould for TCLP test. After the samples were cured for 28 days, the solidified wastes can be taken out by cutting off the plastic before being crushed to the desired size. All these moulds have to be ready before the mixing of OPC, sludge, PFA and  $H_2O$ . When the mixture become homogenous, it will be transferred immediately to the moulds and allowed to set. Plate 4.1 shows the steel mould cubic used for UCS test.

Plate 4.1 Steel mould cubic for UCS test.



#### 4.3.4 Trial Runs

The purpose of trial runs is to examine the workability and durability of cementitious waste mix in various ratios. Since POME sludge was very watery (moisture content of 98.33 %), drying process was required prior to physical properties analysis. From these trial mixes, suitable cement to dry sludge ( $C/S_d$ ) ratios and water to cement ( $W/C$ ) ratios were obtained and then applied in the actual experiment. Besides, some fixed percentages of CRM were chosen to replace the cement in the mixtures. For PMS, a suitable concentration of metals and  $W/C$  ratios were obtained prior the actual experiment.

## **4.4 EXPERIMENTAL PROGRAMS**

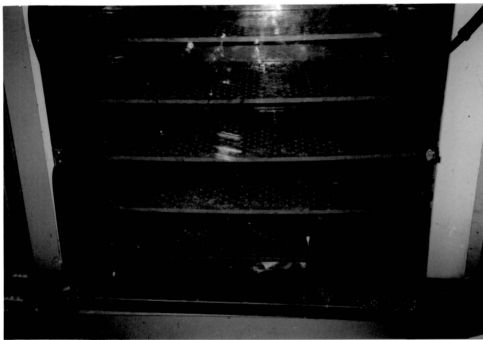
### **4.4.1 Actual Experiment of Runs**

After the completion of preliminary work and trial runs, actual experiments were carried out according to the proposed  $C/S_d$ , PFA percentage and various concentration of metals. Example of calculation for  $C/S_d$  ratios, PFA percentage and concentration of simulated metals are shown in Appendices E and F. The W/C ratio for each mixture also recorded. This is important because the W/C will affect the workability of the mixture and it is determined through the slump test. The mixture is accepted when the slump test gave the value of 8 to 8.5.

### **4.4.2 Treatment of Samples**

Treatment of samples or curing is important in the early stage of hardening in order to obtain good quality of solidified waste. In solidified wastes, normal curing is not applied. Normal curing refers to curing at normal temperature so as to keep it saturated until the originally water filled space in the fresh cement paste has been occupied to the desired extent by the products of hydration of cement. Under dry curing, the samples are treated in dry conditions before compression test and leaching test were carried out. The solidified samples were placed in a cabinet at room temperature (24-30 °C) under control humidity (64 %) to prevent the moisture from evaporating. Plate 4.2 shows the treatment of solidified samples under dry curing conditions.

Plate 4.2 Treatment of solidified samples in a dry curing condition



#### 4.4.3 Filtration

If dissolved metals are to be determined from the leachate, it must be filtered using a preconditioned filtering device containing a filter support of plastic, through an ungridded  $0.45\ \mu\text{m}$  pore diameter membrane filter (polycarbonate or cellulose acetate). During filtration, membrane filters were replaced they become clogged. In filtration, a filter holder capable of supporting of glass fiber filter and able to withstand the pressure needed to accomplish separation was used. The filter holder should be washed prior to use with 10 % nitric acid followed by distilled water. The filtration was carried out at a pressure of 70 to 130 KPa. Plate 4.3 shows the pressure filter units used for filtration of leachate.



Plate 4.3 Pressure filter units used for filtration of leachate



#### 4.5 STANDARD METHODS

"Standard Methods for the Examination of Water and Wastewater" were carried out according to those prepared and published (Greenberg *et al.*, 1992). The procedures and methods described in these standards are intended for the examination of water suitable for domestic or industrial supplies, surface water, ground water, boiler feed water, cooling or circulating water, boiler water, treated and untreated municipal or industrial waste water and saline water. The unit of the fields of water supply, receiving water quality and waste water treatment and disposal is recognized by presenting methods of analysis for each constituent in a single section for all types of water.

An attempt has been made to present methods that apply as generally as possible. Where alternative methods are necessary for samples of different composition, the basis for selecting the most appropriate method is presented as clearly as possible. However, samples with extreme concentrations or otherwise unusual compositions may present difficulties that preclude the direct use of these methods. Hence, some modifications of a procedure may be necessary in specific instance. Most of the methods included here have been endorsed by regulatory agencies. Procedural modification without formal approval may be unacceptable to a regulatory body.

#### 4.5.1 Moisture Content

The procedures of determining the sludge moisture content are as follows:

1. Record the empty container weight, E
2. Fill the empty container with raw sludge, weigh and record weight, C
3. Keep the container with sample in an oven at about 104 °C for 24 hours
4. Weigh the container with sample after dried for 24 hours. Record the weight, D
5. If the sample is in liquid form and contain organic materials, leave in the dry sand bed (heated) before keeping in the oven for 24 hours
6. Measure all masses to the nearest 10 mg

Calculation of moisture content is given by:

$$\text{Moisture content} = \frac{C-D}{C-E}$$

The results of sludge moisture content are given in Appendix C

#### 4.5.2 Specific Gravity

Apparatus : container, a marked flask or bottle to hold a known sludge volume during weighing procedure: Follow 1) or 2)

1. Record sample temperature, T. Weigh empty container and record weight, W. Fill empty container to mark with sample, weigh and record weight, R. measure all masses to the nearest 10mg.
2. If sample got flow readily, add as much of it to container as possible without exerting pressure, record volume, weight and record mass, P. Fill container to mark with distilled water, taking care that air bubbles are not trapped in the sludge or container. Weight and record mass, Q. Measure all masses to nearest 10 mg.
3. The calculation of specific gravity is given by 1) or 2), matching choice of procedure above

i) Specific gravity at 40C = 
$$\frac{\text{Weight of sample}}{\text{Weight of equal volume}}$$
$$= \frac{S - W \times F}{R - W}$$

ii) Specific gravity at 4 °C = 
$$\frac{\text{Weight of sample}}{\text{Weight of equal volume of water at 4 °C}}$$
$$= \frac{(P - W) \times F}{(R - W) - (Q - P)}$$

F is correction factor based on the temperature of the sample. The values of F are given in Table 4.1. The results of sludge specific gravity are shown in Appendix D.

Table 4.1 Temperature Correction Factor, F

Temperature ( $^{\circ}\text{C}$ )	Temperature Correction Factor, F
15	0.9991
20	0.9982
25	0.9975
30	0.9957
35	0.9941
40	0.9922
45	0.9903

#### 4.5.3 Nitric Acid Digestion

Apparatus : Hot plate, conical flask, 125 ml or Griin beakers, 150 ml acid washed and rinse with water.

Reagents : Nitric acid,  $\text{HNO}_3$  (concentrated)

Procedure:

1. Mix samples and transfer a suitable volume (50 ml) to a 125 ml conical flask or beaker.
2. Add 5 ml concentrated  $\text{HNO}_3$  and a few boiling chips, glass beads or Hengar granules.
3. Bring to a slow boil and evaporate on a hot plate to the lowest volume possible (about 10 to 20 ml) before precipitation occurs. Continue heating and adding concentrated  $\text{HNO}_3$  as necessary until digestion is completed as shown by a light-colored, clear solution. Do not sample dry during digestion.
4. Wash down flask or beaker walls with water and then filter if necessary. Transfer filtrate to a 100 ml volumetric flask with two 5 ml portion of water, adding these rinsing to the volumetric flask.

5. Cool, dilute to mark and mix thoroughly. Take portion of this solution for required metal determination. Alternatively, take a larger sample volume through the procedure for concentration.

#### **4.6 METAL DETERMINATION BY ICP-OES MACHINE**

The concentration of heavy metal in raw sludge and in leachate can be determined by using inductive coupled plasma (ICP). In these studies, total metals of raw sludge were determined after appropriate digestion with nitric acid. Meanwhile, the metals concentration in leachate for the treated waste was determined in filtered and acidified samples. ICP technique was developed in the mid-1960's as a rapid, sensitive and convenient method for the determination of metals in water and wastewater samples. An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field typically oscillating at 27.1 MHz. This field is inductively coupled to the ionized gas by a water-cooled surrounding the quartz "torch" that supports and confines the plasma. A sample aerosol is generated in an appropriate nebulizer injector tube located within the torch.

The sample aerosol is injected directly into the ICP, subjecting the constituent atoms to temperatures of 6000 to 8000 K. As this result in almost complete dissociation of molecules, significant reduction in chemical interference is achieved. The high percentage of the plasma excites atomic efficiently. Ionization of high percentage of atomic procedures ionic emission spectra. The efficient excitation provided by ICP results in low detection limits for many elements. This coupled with the extended dynamic range, permits effective multi element determination of metals.

## **4.7 COMPRESSIVE STRENGTH STUDIES**

The unconfined compressive strength test is the simplest and reliable method for testing of hardened products. The strength development affects the possibility of using these stabilized/solidified products as reused waste materials like as a fill for land reclamation, drainage and road pavement. In these studies, the unconfined strength test had been carried out to gauge the strength of the final products. In this study, the effects of curing and C/S<sub>d</sub> ratio on the strength development can be investigated.

### **4.7.1 Preparation of Solidified Waste**

Solidified samples were prepared according to the proposed C/S<sub>d</sub> ratios and percentage of PFA. For pure model study, the solidified samples were prepared according to various concentrations of metals. The sludge was first homogenizing with an electric blender (see Plate 4.4) for 2-3 minutes. During mixing, cement was slowly added and CRM were added after the cement addition and mixed for a further 5 minutes. Then distilled water was added slowly to the electric blender until the mixture appeared homogenous and a suitable workability obtained. For pure model study, various metals concentration were added to the cement and mixed for a further 5 minutes.

A slump test was used to test the workability. A suitable workability was indicated by the slump test readings at 8 to 8.5. After the homogenous slurries were obtained, the slurries were quickly casted into 50 mm x 50 mm x 50 mm cube moulds for UCS test and 1 litre plastic container for TCLP test. Casting was done in 3 layers with each layer compacted using vibrating table (see Plate 4.5) to yield good packing. The mould were then cured at room temperature (25 to 33 °C) and 92 % relative humidity. Perspex covers were used to cover the moulds to prevent excessive loss of water by evaporation. After 24 hours, the cubes were demoulded and put into a cabinet for further dry curing. Plate 4.6 shows the solidified samples which were ready for UCS test.

Plate 4.4 Electric blender used to prepare the mixture

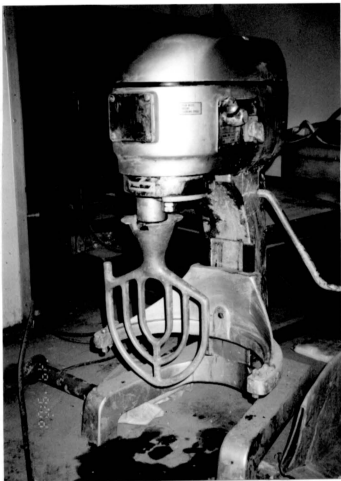
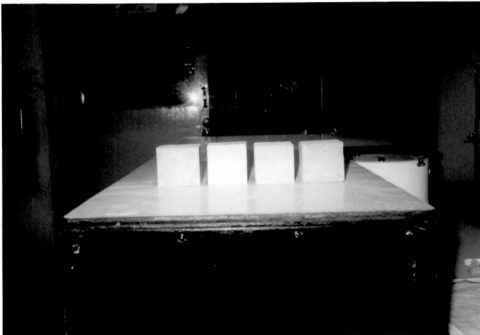


Plate 4.5 Vibration table for compaction



Plate 4.6 The solidified samples for UCS test





#### **4.7.2 Unconfined Compressive Strength Test (UCS)**

The UCS test measures the shear strength of a cohesive, soil-like material in unsaturated undrained conditions without lateral confinement on the sample. The test method provides an approximate value of the strength of treated waste in terms of total stress. The treated waste may be undisturbed, remould or recompacted. The test is applicable to cohesive materials that do not expel water during the loading portion of the test.

#### **4.7.3 Testing Description**

The dimension of cured samples was measured to get the surface area before being tested for their UCS. The test was completed by centering a sample on the machine containing upper and lower plates and the sample is not supported laterally. The two sides of the samples in contact with the compression machine were lined up with steel plates, in order to have a plane surface and equal applied on the cube. The determination of compressive strength is by compressing the samples until they were broken and the value read off from a scale meter of the machine.

Testing has been done by using compressive strength testing machine. Plate 4.7 shows the compressive strength test machine. Samples according to different C/S<sub>a</sub> ratios and percentages of PFA added (refer to Appendix E) and various concentration of metals for pure model study (refer to Appendix F) were tested separately after they were cured for 1, 3, 7, 14, 28 and 56 days in order to get their strength development. Triplicate samples were tested to obtain more representative results.

Plate 4.7 Compressive Strength Test Machine



## **4.8 LEACHING STUDIES**

In this study, crushed block leaching was carried out to simulate the leaching behaviours of solidified products in landfill under neutral and acidic environment. Crushed block leaching tends to display a longer or extended leaching after the samples were broken down.

### **4.8.1 Preparation of Solidified Waste**

The procedures for preparing the solidified waste are the same as the procedures for preparing the solidified waste for compressive strength studies.

### **4.8.2 Crushed Block Leaching (CBL)**

Crushed block leaching basically involves crushing of solidified waste to a surface area gram of material equal or greater than  $3.1 \text{ cm}^2$  or to consist of particles smaller than 9.52 mm in their narrowest dimension. The solidified sample in the 1 litre plastic container was cut off and crushed after 28 days of curing period. The crushed particles was then allowed to pass through a 9.52 mm sieve to get the particle with the desired size. The crushed solids were then mixed with the leaching extractant for a given period of time. In this crushed block leaching, TCLP was conducted to produce the leachate for contaminants analysis.

#### **4.8.2.1 Method 1311 - Toxicity Characteristic Leaching Procedure (TCLP)**

For regulatory and remediation purposes a standard test is needed to measure the likelihood of toxic substances getting into the environment and causing harm to organisms. The test required by the USEPA is Method 1311-Toxicity Characteristic Leaching Procedure (TCLP) designed to determine the mobility of both organic and inorganic contaminants is present in liquid, solid and multi-phases wastes. For analysis of toxic species a solution is leached from the waste and is designated as the TCLP

extract. If no significant solid material is present, the waste is filtered through a 0.6 - 0.8  $\mu\text{m}$  glass fibre filter and designated as the TCLP extract. In mixed liquid-solid wastes the liquid is separated and analysed separately.

#### 4.8.2.1.1 Testing Description

TCLP was conducted as a test to examine the concentration of contaminants in the leachate. In TCLP the test was applied to the crushed 9.52mm sized stabilized/solidified samples using two types of leachant;

1. 0.5 M acetic acid ( $\text{pH} = 2.85 \pm 0.05$ ) for contaminant analysis
2. deionized water ( $\text{pH} = 6.5$  to  $6.8$ ) for COD analysis

Firstly, the solidified and stabilized samples were crushed and separated by sieving to 9.52 mm. Then 100 gm of the sieve samples was used to give a ratio of 20:1 mass ratio of extractant liquid to solid sample. The 100 gm crushed samples were placed in extractor bottles containing 2 litres of extraction fluids (acetic acid or deionized water). The 0.5 M acetic acid solution can be prepared by diluting 11.4 mL gracial  $\text{CH}_3\text{COOH}$  with reagent water to a volume of 2 litres. These extraction fluids should be monitored frequently for impurities. The  $\text{pH}$  ( $2.88 \pm 0.05$ ) should be checked prior to use to ensure that these fluids are made up accurately. Vigorous mixing was then carried out in a special rotary extractor at  $30 \pm 2$  rpm (see plate 4.8) at room temperature for  $18 \pm 2$  hours. The  $\text{pH}$  of the extract was measured by using a  $\text{pH}$  meter at the end of the extraction period prior to filtration by using a  $0.45 \mu\text{m}$  Whatman membrane filter. The collected TCLP extract after filtration is known as stabilized/solidified waste leachate. The leachate was preserved for heavy metal analyses on the OCP-OES. The leachate must be acidified for  $\text{pH} < 2$  by using nitric acid. All other leachate must be stored in plastic bottles under refrigeration at  $40^\circ\text{C}$  until analyzed.

Plate 4.8 Rotary Agitation Apparatus



#### 4.8.3 Leachate Analysis and Testing

In this study, the types of contaminant analysed were toxic metals such as iron, copper and zinc. The dissolved metals mentioned above had been tested by ICP-OES at the Public Health Laboratory, Department of Civil Engineering and the method applied is according to that discussed in section 4.6. Comparison of toxicity characteristic constituents is given in Table 4.2 . Table 4.3 shows the solidified waste acceptance criteria by waste disposal authority.

Table 4.2 Toxicity Characteristic Constituents (USEPA, 1990)

EPA HW No.	Constituents	Chronic Toxicity (mg/L)	Regulatory Level (mg/L)
D008	Lead	0.05	5.0
**	Iron	**	5.0
**	Copper	**	5.0
**	Zinc	**	5.0

\*\* - Based on UK Waste Disposal Authority

Table 4.3 Specimen solidified waste performance characteristics as required by waste disposal authority (Sollars and Perry, 1989)

Characteristic	Requirement	Comparative Values
Compressive Strength (28 days)	$> 0.34 \text{ MN/m}^2$	Concrete : $30 \text{ MN/m}^2$ Mortar : $20 \text{ MN/m}^2$ Grouts : $0.5 - 4 \text{ MN/m}^2$
Permeability (28 days)	$> 1 \times 10^{-7}$	Concrete : $1 \times 10^{-8}$ Sand : $1 \times 10^{-4} - 5 \times 10^{-5} \text{ m/s}$ Silt : $1 \times 10^{-6} - 1 \times 10^{-7} \text{ m/s}$ Clay : $10^{-8} - 10^{-10} \text{ m/s}$
Leachate Quality	pH 8 – 11 Toxic heavy metals: Zn $< 10 \text{ g/m}^3$ , Hg $< 0.5 \text{ g/m}^3$ Others (Cd, Cr, Cu, Ni, Pb, Ba, Co, V, Mb, Sn, As, Se, Sb), $5 \text{ g/m}^3$	-NA-

$1 \text{ MN/m}^2 = 1 \text{ N/mm}^2$  NA – not applicable