



STABILIZATION AND SOLIDIFICATION OF PALM
OIL MILL EFFLUENT SLUDGE AND A PURE
MODEL STUDY USING CEMENTITIOUS
TECHNIQUE

NOR ASIKIR BINTI MAMAT

INSTITUTE OF POSTGRADUATE STUDIES (IPS)
UNIVERSITY OF MALAYA
DECEMBER 2002

**STABILIZATION AND SOLIDIFICATION OF PALM OIL MILL EFFLUENT
SLUDGE AND A PURE MODEL STUDY USING CEMENTITIOUS
TECHNIQUE**

NOR ASIKIR BINTI MAMAT

Dissertation submitted in partial fulfillment of the requirements for the Degree
of Master of Technology (Environmental Management)

Institute of Postgraduate Studies (IPS)
University of Malaya
50603 Kuala Lumpur

December 2002

Perpustakaan Universiti Malaya



A510227828

OK

ABSTRACT

This research studies the effectiveness of using method of stabilization and solidification (S/S) to palm oil mill effluent (POME) sludge as a pretreatment method prior to ultimate disposal to land and to investigate the effect of varying the concentration of simulated metals (zinc, copper and iron) for pure model study (PMS). The characteristics of the solidified products including unconfined compressive strength (UCS) and toxicity characteristic leaching procedure (TCLP) from USEPA were evaluated. The influence of cement replacement material (CRM), namely pulverized fly ash (PFA) on the effectiveness of S/S was also investigated for POME sludge.

The POME sludge was stabilized using ordinary portland cement (OPC) with cement-dry sludge (C/S_d) ratios of 6, 7, 8, 9 and 10. PFA was used to replace cement at 5 %, 10 %, 15 %, and 20 % based on evaluated C/S_d ratios. For PMS, the metals of concern were copper, iron and zinc. The concentrations of copper used were 7 ppm, 34 ppm, 133 ppm, 228 ppm and 321 ppm. For iron, the concentrations used were 7 ppm, 34 ppm, 133 ppm, 230 ppm and 323 ppm while the concentrations of zinc used were 7 ppm, 34 ppm, 134 ppm, 232 ppm and 327 ppm. The strengths of the solidified sludge were obtained at 1, 3, 7, 14, 28 and 56 days.

Toxicity characteristic leaching procedure (TCLP) was performed after 28 days of curing. Two types of leachant were used to study the leaching mechanism of treated

sludge, namely 0.5M acetic acid (HAc, pH=2.89) and deionised water (pH=7.1). Metals of concern were lead, copper, zinc and iron. Metals were determined by using inductive couple plasma (ICP). UCS results showed that the strength increased with increasing of C/S_d ratios and proportion of PFA. Sample of C/S_d of 10 and containing 20% PFA gave the best UCS result of 3.38 N/mm² at 56 days. The UK legal limit for UCS is 0.34 N/mm².

The leachate analysis has indicated that all the samples comply with the regulatory requirement of metal concentration of 5 ppm. From the analysis, the sample with C/S_d ratio of 10 and 20 % PFA addition can be considered as the most suitable mix design to be adopted. For PMS, metals concentration of 34 ppm gave the best UCS results for all metals. It was observed that the presence of inorganic materials decreased the strength of OPC and increased the amount of metals released in leaching studies.

ABSTRAK

Kajian ini dijalankan bagi menyelidik keberkesanan menggunakan kaedah pemejalan dan penstabilan ke atas enapcemar kelapa sawit sebagai kaedah pra-perawatan sebelum dibuang ke tapak pelupusan dan mengkaji kesan mempelbagaikan kepekatan logam-logam simulasi iaitu zink, kuprum dan besi. Sifat-sifat produk yang dipejalkan telah dikaji dengan menggunakan ujian-ujian seperti kekuatan mampatan dan pengurusan. Bagi enapcemar kelapa sawit, pengaruh bahan penggantian simen iaitu abu terbang (PFA) telah dikaji ke atas keberkesanan penstabilan dan pemejalan.

Enapcemar kelapa sawit telah distabilkan menggunakan simen portland biasa (OPC) dengan nisbah simen-enapcemar kering (C/S_d), 6, 7, 8, 9, 10. Abu terbang telah diguna untuk menggantikan simen dengan peratusan 5 %, 10 %, 15 %, 20 % berdasarkan nisbah C/S_d . Bagi kajian model tulen (PMS), logam-logam yang dikaji adalah kuprum, besi dan zink. Kepekatan kuprum yang digunakan adalah 7 ppm, 34 ppm, 133 ppm, 228 ppm dan 321 ppm. Bagi besi, kepekatan yang digunakan adalah 7 ppm, 34 ppm, 133 ppm, 230 ppm dan 323 ppm sementara kepekatan zink adalah 7 ppm, 34 ppm, 134 ppm, 232 ppm and 327 ppm. Kekuatan bagi enapcemar dan logam simulasi telah dilakukan pada usia pengawetan 1, 3, 7, 14, 28 dan 56 hari.

Ujian pengurusan telah dijalankan selepas 28 hari usia pengawetan. Ujian kurasan telah dilakukan dalam dua medium iaitu 0.5 M asid asetik ($pH=2.89$) dan air suling ($pH=7.1$). Kandungan logam telah dianalisis dengan menggunakan plasma terganggu induktif (ICP). Keputusan ujian mampatan menunjukkan bahawa

kekuatan meningkat dengan peningkatan C/S_d dan kandungan PFA. Had undang-undang UK bagi ujian kekuatan ialah 0.34 N/mm^2 .

Analisis kurasan menunjukkan yang semua sampel mematuhi kehendak undang-undang dengan kepekatan logam 5 ppm. Dari analisis juga menunjukkan campuran dengan nisbah C/S_d 10 dan 20 % PFA memberikan kekuatan tertinggi. Untuk PMS, kekuatan tertinggi dicapai pada kepekatan logam 34 ppm bagi ketiga-tiga logam. Berdasarkan kajian ini didapati kehadiran bahan-bahan tak organik boleh mengurangkan kekuatan OPC dan meningkatkan jumlah logam yang terkuras keluar.

ACKNOWLEDGEMENT

First and foremost my prayer and glory be to Allah SWT, the most Gracious and Most Merciful, for given me the strength and ability towards the completion of this thesis report.

In the process of completing this thesis, my gratitude goes to various people who have helped in making this project successful. My heartfelt appreciation goes to my supervisors, Associate Professor Dr Md Ghazaly Shaaban and Associate Professor Dr Hilmi Mahmud, from Department of Civil Engineering, for being very patience in their advice, constructive criticisms and comments. Their constant supervisions and guidance are indeed very helpful and invaluable.

I also wish to thank Mrs Kalaiselvi and Puan Halipah, the laboratory assistants at Public Health Laboratory, who had graciously helped to provide materials and apparatus needed for my experiment.

Last but not least, I would like to convey my deepest gratitude and special thanks to my beloved parents and family for their patience, support, advice and constant prayer when I needed most at time of hardship which finally lead to success. For Dr Samsudin Taib, En Rosdi Ismail and Pn Enid, thank you for being there when I am in need.

TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	iii
ACKNOWLEDGEMENT	v
TABLE OF CONTENTS	vi
LIST OF APPENDICES	xiii
LIST OF FIGURES	xv
LIST OF PLATES	xix
LIST OF TABLES	xx
SYMBOLS AND ABBREVIATIONS	xxi
CHAPTER	
1 INTRODUCTION	1
1.1 General	1
1.2 A Brief Introduction of Palm Oil Industry	2
1.3 The Processing of Palm Oil	3
1.4 Palm Oil and Environment	6
1.5 Stabilization and Solidification (S/S)	8
1.6 Pure Model Study	9
2 LITERATURE REVIEW	11
2.1 Waste Treatment Technologies	11
2.1.1 Biological Methods	11
2.1.1.1 Conventional Treatment	11
2.1.1.2 In-situ Bioremediation	12

2.1.2	Solid-Phase Treatment	12
2.1.3	Physico-Chemical Process	12
2.1.3.1	Air Stripping	13
2.1.3.2	Soil Vapor Extraction (SVE)	13
2.1.3.3	Carbon Adsorption	13
2.1.4	Thermal Method	14
2.1.5	Stabilization and Solidification (S/S)	14
2.2	Treatment Methods for POME Sludge	15
2.3	Comparison of S/S Technique with Ponding and Tank Digester Systems	20
2.4	The Economics of S/S Compared to Ponding and Tank Digester Systems	24
2.5	Previous Studies on POME Utilization	27
2.6	Current Stabilization and Solidification Process	28
2.6.1	Organic Process	29
2.6.1.1	Thermoplastic Technique	29
2.6.1.2	Organic Polymer Technique	30
2.6.1.3	Encapsulation Technique	30
2.6.2	Inorganic Process	30
2.6.2.1	Cement-based Technique	31
2.6.2.2	Lime-based Technique	33
2.7	Stabilization and Solidification (S/S) Mechanisms	33
2.7.1	Macroencapsulation	34
2.7.2	Microencapsulation	34
2.7.3	Embedment	34
2.8	Factors Affecting Stabilization and Solidification Process	35

2.8.1	Physical Factors	35
2.8.1.1	Particle Size and Distribution	35
2.8.1.2	Particle Morphology	36
2.8.1.3	Flash Point	37
2.8.1.4	Free Water Content	37
2.8.1.5	Solid Content	37
2.8.1.6	Specific Gravity	37
2.8.1.7	Viscosity	38
2.8.1.8	Temperature and Humidity	38
2.8.2	Chemical Factors	38
2.8.2.1	Alkalinity and Acidity	39
2.8.2.2	Composition and Speciation	39
2.8.2.3	Zeta Potential	39
2.8.2.4	Redox Potential	40
2.9	Advantages and Disadvantages of Stabilization and Solidification	40
2.10	Local Studies on S/S Technique	42
2.11	Binders and Binding Mechanisms	46
2.11.1	Inorganic Binders	47
2.12	Materials for Stabilization and Solidification	47
2.12.1	Cement	47
2.12.2	Pozzolan Materials	48
2.12.3	Silicate Materials	48
2.13	Effects of Organic Wastes on Cement/Pozzolan System	49

2.14	Cement Setting and Hydration	50
2.15	Cement-Replacement Materials	54
2.15.1	Pulverized Fly Ash (PFA)	54
2.15.2	Rice Husk Ash (RHA)	55
2.16	Heavy Metals	55
2.17	Previous Studies on Unconfined Compressive Strength (UCS)	57
2.18	Leaching Mechanisms	57
2.18.1	Previous Studies on Leaching	57
2.18.2	Toxicity Characteristic Rules	58
2.19	Leaching Testing	59
2.19.1	Toxicity Characteristic Leaching Procedure (TCLP)	59
2.19.2	Synthetic Acid Precipitation Leach Test (SAPLT)	59
2.19.3	Shake Extraction Test (SET)	60
2.19.4	Sequential Leach Test (SLT)	60
2.19.5	Sequential Chemical Extraction (SCE)	60
2.19.6	Multiple Extraction Procedure (MEP)	60
2.19.7	Monofilled Waste Extraction Procedure (MWEP)	61
2.19.8	Equilibrium Leach Test (ELT)	61
2.19.9	American Nuclear Society Leach Test (ANSLT)	61
2.19.10	Dynamic Leach Test (DLT)	61
3	OBJECTIVES OF THE THESIS	62
3.1	Objectives of Study	62
4	MATERIALS AND METHODS	63
4.1	Objectives	63
4.1.1	Leaching Test	63

4.1.2	Compressive Strength Test	64
4.2	Program Schedule	65
4.2.1	Preliminary Work	65
4.2.2	Laboratory Studies	65
4.2.3	Data Analysis	66
4.2.4	Report Writing	66
4.3	Preliminary Work and Preparation of Materials	66
4.3.1	Sludge Moisture Content	66
4.3.2	Sludge Specific Gravity	67
4.3.3	Preparation of Moulds	67
4.3.4	Trial Runs	68
4.4	Experimental Programs	69
4.4.1	Actual Experimental Runs	69
4.4.2	Treatment of Samples	69
4.4.3	Filtration	70
4.5	Standard Methods	71
4.5.1	Moisture Content	72
4.5.2	Specific Gravity	72
4.5.3	Nitric Acid Digestion	74
4.6	Metal Determination by ICP-OES Machine	75
4.7	Compressive Strength Studies	76
4.7.1	Preparation of Solidified Waste	76
4.7.2	Unconfined Compressive Strength Test (UCS)	79
4.7.3	Testing Description	79
4.8	Leaching Studies	81
4.8.1	Preparation of Solidified Waste	81

	4.8.2	Crushed Block Leaching (CBL)	81
	4.8.2.1	Method 1311-Toxicity Characteristic Leaching Procedure (TCLP)	81
	4.8.2.1.1	Testing Description	82
	4.8.3	Leachate Analysis and Testing	83
5		RESULTS AND DISCUSSIONS	85
	5.1	Raw Palm Oil Mill Effluent (POME) Sludge	85
	5.1.1	Moisture Content	85
	5.1.2	Specific Gravity	85
	5.2	Characteristics of Heavy Metals in Raw Palm Oil Mill Effluent (POME) Sludge	86
	5.3	Water-Cement Ratio (W/C)	88
	5.4	Development of Unconfined Compressive Strength UCS)	88
	5.4.1	Influence of Cement-Dry sludge Ratio (C/S_d)	89
	5.4.2	Influence of Various Concentrations of Simulated Metals for Pure Model Study	92
	5.4.2.1	Iron	93
	5.4.2.2	Zinc	94
	5.4.2.3	Copper	95
	5.4.3	Influence of Cement Replacement Material (CRM) – Pulverized Fly Ash (PFA)	97
	5.4.4	Influence of Curing Age on Solidified Sample	100
	5.4.5	Effects of Organic and Inorganic on Ordinary Portland Cement and Pozzolanic System	103
	5.4.6	Relationships of UCS, C/S_d and Curing Age	104
	5.4.7	Relationships of UCS, Simulated Metal Concentration	

	and Curing Age	105
	5.4.8 Overview of the Result of UCS	105
5.5	Leachability and Leachate Quality	114
	5.5.1 pH of TCLP Extracts	114
	5.5.2 Leachate Analysis Contaminant	117
	5.5.3 Summary of the Results of Leachability	123
	5.5.4 Relationship Between Compressive Strength and Leachability	123
6	CONCLUSIONS AND RECOMMENDATIONS	135
	6.1 Conclusions	135
	6.1.1 Unconfined Compressive Strength	135
	6.1.2 Crushed Block Leaching	135
	6.2 Recommendations	137
	REFERENCES	138

LIST OF APPENDICES

	Page
Appendix A: Casting Date and Curing Age of Solidified POME Sludge Samples for UCS and TCLP	A1
Appendix B: Casting Date and Curing Age of Solidified Simulated Metals for UCS and TCLP	A2
Appendix C: Moisture Content	A3
Appendix D: Specific Gravity	A4
Appendix E: Sample Calculation for C/S_d	A5
Appendix F: Example Calculation for Various Simulated Metals Concentration	A7
Appendix G: Weight of Materials at Various C/S_d Ratios	A12
Appendix H: Unconfined Compressive Strength (UCS) on Various Days for OPC + POME Sludge + 0 % PFA	A13
Appendix I: Unconfined Compressive Strength (UCS) on Various Days for OPC + POME Sludge + 5 % PFA	A18
Appendix J: Unconfined Compressive Strength (UCS) on Various Days for OPC + POME Sludge + 10 % PFA	A23
Appendix K: Unconfined Compressive Strength (UCS) on Various Days for OPC + POME Sludge + 15 % PFA	A28
Appendix L: Unconfined Compressive Strength (UCS) on Various Days for OPC + POME Sludge + 20 % PFA	A33
Appendix M: Unconfined Compressive Strength (UCS) on Various Days for OPC + Copper	A38

Appendix N: Unconfined Compressive Strength (UCS) on Various Days for OPC + Iron	A43
Appendix O: Unconfined Compressive Strength (UCS) on Various Days for OPC + Zinc	A48
Appendix P: Leaching of Heavy Metals of POME Sludge of TCLP Method in HAc Leachant	A52
Appendix Q: Leaching of Heavy Metals of POME Sludge of TCLP Method in DW Leachant	A53
Appendix R: Leaching of Heavy Metals of POME Sludge of TCLP Method in HAc Leachant	A54
Appendix S: Leaching of Heavy Metals of POME Sludge of TCLP Method in DW Leachant	A55
Appendix T: pH of POME Sludge Extracts of TCLP in HAc Leachant	A56
Appendix U: pH of POME Sludge Extracts of TCLP in DW Leachant	A57
Appendix V: pH of Solidified Simulated Metals Extracts of TCLP In HAc Leachant	A58
Appendix W: pH of Solidified Simulated Metals Extracts of TCLP In DW Leachant	A59

LIST OF FIGURES

	Page
1.1 Schematic Flow Diagram of Palm Oil Process	5
2.1 Schematic Flow Diagram for Ponding System	16
2.2 Schematic Flow Diagram of Tank Digester and Extended Aeration System	18
2.3 Schematic Flow Diagram of Closed Anaerobic Digester and Land Application System	19
5.1 Unconfined Compressive Strength (UCS) Development for Various C/S_d , 0 % PFA	91
5.2 Unconfined Compressive Strength (UCS) Development for Various C/S_d , 5 % PFA	91
5.3 Unconfined Compressive Strength (UCS) Development for Various C/S_d , 10 % PFA	91
5.4 Unconfined Compressive Strength (UCS) Development for Various C/S_d , 15 % PFA	92
5.5 Unconfined Compressive Strength (UCS) Development for Various C/S_d , 20 % PFA	92
5.6 Unconfined Compressive Strength (UCS) Development for Various Concentration of Iron	94
5.7 Unconfined Compressive Strength (UCS) Development for Various Concentration of Copper	95
5.8 Unconfined Compressive Strength (UCS) Development for Various Concentration of zinc	96
5.9 Unconfined Compressive Strength (UCS) Development for $C/S_d = 6$	98

5.10	Unconfined Compressive Strength (UCS) Development for $C/S_d = 7$	99
5.11	Unconfined Compressive Strength (UCS) Development for $C/S_d = 8$	99
5.12	Unconfined Compressive Strength (UCS) Development for $C/S_d = 9$	99
5.13	Unconfined Compressive Strength (UCS) Development for $C/S_d = 10$	100
5.14	Unconfined Compressive Strength (UCS) Development for Various Percentages of PFA at 1 Day of Curing Age	101
5.15	Unconfined Compressive Strength (UCS) Development for Various Percentages of PFA at 3 Day of Curing Age	
5.16	Unconfined Compressive Strength (UCS) Development for Various Percentages of PFA at 7 Day of Curing Age	101
5.17	Unconfined Compressive Strength (UCS) Development for Various Percentages of PFA at 14 Day of Curing Age	102
5.18	Unconfined Compressive Strength (UCS) Development for Various Percentages of PFA at 28 Day of Curing Age	102
5.19	Unconfined Compressive Strength (UCS) Development for Various Percentages of PFA at 56 Day of Curing Age	102
5.20	Unconfined Compressive Strength (UCS) Development for Various $C/S_d + 0\%$ PFA	106
5.21	Unconfined Compressive Strength (UCS) Development for Various $C/S_d + 5\%$ PFA	107
5.22	Unconfined Compressive Strength (UCS) Development for Various $C/S_d + 10\%$ PFA	108

5.23	Unconfined Compressive Strength (UCS) Development for Various C/S _d + 15 % PFA	109
5.24	Unconfined Compressive Strength (UCS) Development for Various C/S _d + 20 % PFA	110
5.25	Unconfined Compressive Strength (UCS) Development for Various Concentrations of Copper	111
5.26	Unconfined Compressive Strength (UCS) Development for Various Concentrations of Zinc	112
5.27	Unconfined Compressive Strength (UCS) Development for Various Concentrations of Iron	113
5.28	pH of DW Extracts of TCLP for Various C/S _d Ratio	115
5.29	pH of HAc Extracts of TCLP for Various C/S _d Ratio	116
5.30	pH of HAc Extracts of TCLP for Pure Model study	116
5.31	pH of DW Extracts of TCLP for Pure Model Study	116
5.32	Leaching of Copper in HAc Leachant	118
5.33	Leaching of Copper in DW Leachant	118
5.34	Leaching of Iron in HAc Leachant	119
5.35	Leaching of Iron in DW Leachant	119
5.36	Leaching of Zinc in HAc Leachant	120
5.37	Leaching of Zinc in DW Leachant	120
5.38	Leaching of Iron in HAc Leachant for Various Simulated Metals	121
5.39	Leaching of Iron in DW Leachant for Various Simulated Metals	121
5.40	Leaching of Zinc in HAc Leachant for Various Simulated Metals	121
5.41	Leaching of Zinc in DW Leachant for Various Simulated Metals	122
5.42	Leaching of Copper in HAc Leachant for Various Simulated Metals	122
5.43	Leaching of Copper in DW Leachant for Various Simulated Metals	122

5.44	Relationship Between 28-Days UCS and Iron Leachability for 0 % PFA in HAc Leachant	125
5.45	Relationship Between 28-Days UCS and Iron Leachability for 0 % PFA in DW Leachant	126
5.46	Relationship Between 28-Days UCS and Iron Leachability for 5 % PFA in HAc Leachant	127
5.47	Relationship Between 28-Days UCS and Iron Leachability for 5 % PFA in DW Leachant	128
5.48	Relationship Between 28-Days UCS and Iron Leachability for 10 % PFA in HAc Leachant	129
5.49	Relationship Between 28-Days UCS and Iron Leachability for 10 % PFA in DW Leachant	130
5.50	Relationship Between 28-Days UCS and Iron Leachability for 15 % PFA in HAc Leachant	131
5.51	Relationship Between 28-Days UCS and Iron Leachability for 15 % PFA in DW Leachant	132
5.52	Relationship Between 28-Days UCS and Iron Leachability for 20 % PFA in HAc Leachant	133
5.53	Relationship Between 28-Days UCS and Iron Leachability for 20 % PFA in DW Leachant	134

LIST OF PLATES

	Page
4.1 Steel Mould Cubic for Unconfined Compressive Strength (UCS)	68
4.2 Treatment of Solidified Samples in a Day Curing Condition	70
4.3 Pressured Filter Unit for Filtration of Leachate	71
4.4 Electric Blender Used to Prepare the Mixture	77
4.5 Vibration Table for Compaction	78
4.6 The Solidified Samples for Unconfined Compressive Strength Test	78
4.7 Compressive Strength Test Machine	80
4.8 Rotary Agitation Apparatus	83
5.1 Raw POME Sludge	87

LIST OF TABLES

	Page
1.1 POME Discharge Standards	8
2.1 Comparison Between S/S Technique with Present POME Treatment Methods	20
2.2 Present and Projected Economic Consideration for S/S Technique	25
2.3 Economic Analysis of the Ponding and Tank Digester System	26
2.4 Advantages and Disadvantages of Various Stabilization and Solidification Process	41
4.1 Temperature Correction Factor, F	74
4.2 Toxicity Characteristic Constituents	84
4.3 Specimen Solidified Waste Performance Characteristics as Required by Waste Disposal Authority	84
5.1 Characteristics of Raw Palm Oil Mill Effluent Sludge	87
5.2 The compressive Strength of Cement-Paste for W/C = 0.34	104

SYMBOLS AND ABBREVIATIONS

ANSLT	-	American nuclear society leach test
BOD	-	Biological oxygen demand
CPO	-	Crude palm oil
CBL	-	Crushed block leaching
C-S-H	-	Calcium silica hydrate
CRM	-	Cement replacement material
C/Sd	-	Cement to dry sludge ratio
DLT	-	Dynamic leach test
DW	-	Deionized water
DOE	-	Department of Environment
EP	-	Extraction procedure
EPA	-	Environment Protection Agency
ELT	-	Equilibrium leach test
GAC	-	Granular activated carbon
HAc	-	Acetic acid
HDPE	-	High density polyethylene
ICP-OES	-	Inductively coupled plasma-Optical emission spectrometry
JIS	-	Japanese Institute of Standard
MC	-	Moisture content
MEP	-	Multiple extraction procedure
MWEP	-	Monofilled waste extraction procedure
OPC	-	Ordinary Portland cement
POME	-	Palm Oil Mill effluent

PFA	-	Pulverised fly ash
RCRA	-	Resource, Recovery and Conservation Act
SG	-	Specific gravity
S/S	-	Stabilization and solidification
SET	-	Shake extraction test
SAPLT	-	Synthetic and precipitation leach test
SLT	-	Sequential leach test
SVE	-	Soil vapor extraction
TCLP	-	Toxicity Characteristic Leaching Procedure
UCS	-	Unconfined compressive strength
VOC	-	Volatile organic compound
W/C	-	Water to cement ratio