EVALUATION OF SOLIDIFIED AND STABILIZED SHIPYARD ABRASIVE BLASTING WASTE AS CONSTRUCTION MATERIAL

SALMALIZA BINTI SALLEH

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2018

EVALUATION OF SOLIDIFIED AND STABILIZED SHIPYARD ABRASIVE BLASTING WASTE AS CONSTRUCTION MATERIAL

SALMALIZA BINTI SALLEH

THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2018

UNIVERSITY OF MALAYA
ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: SALMALIZA BINTI SALLEH

Matric No: KHA 090054

Name of Degree: DOCTOR OF PHILOSOPHY

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

EVALUATION OF SOLIDIFIED AND STABILIZED SHIPYARD ABRASIVE BLASTING WASTE AS CONSTRUCTION MATERIAL.

Field of Study: CONSTRUCTION TECHNOLOGY AND MANAGEMENT

I do solemnly and sincerely declare that:

(1) I am the sole author/writer of this Work;
(2) This Work is original;
(3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
(4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
(5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
(6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate's Signature Date:

Subscribed and solemnly declared before,

Witness's Signature Date:

Name:

Designation:

EVALUATION OF SOLIDIFIED AND STABILIZED SHIPYARD ABRASIVE BLASTING WASTE AS CONSTRUCTION MATERIAL

ABSTRACT

Tons of abrasive blasting wastes (ABW) are produced each year from the removal of old paint from the ships. The abrasives contain heavy metals which are considered hazardous by the Toxicity Characteristic (TC) criteria. This research describes an investigation of cement-based solidification and stabilization (S/S) of the spent abrasives from ship repair, which is mainly spent copper slag. ABW which are mixed with Ordinary Portland cement (OPC) ranging from ratio of 0 to 1.5 by weight of cement were tested for crushed block leachability and compressive strength. The water-to-cement ratio of the mixes was set at 0.35 to 0.5. The results indicated that the leaching of selected heavy metal ions from the cement matrix was low and did not exceed the United States Environmental Protection Agency (US EPA) and Malaysian Department of Environment (DOE) Regulation Guidelines. However, addition of abrasive blasting waste to cement increased the initial setting times, which retards the process of hardening of the cement matrix. The strength of the S/S abrasives was generally lower than the control cement paste. Optimum strength achieved when the ratio of C/ABW is 1.5 with water-to-cement ratio of 0.35. In the next stage of study, sand was added in the cement-ABW matrix to develop bricks for construction purpose. The strength of the C/ABW bricks was generally higher than the control and conventional sand-cement bricks. The optimum strength achieved when 20% of sand weight was replaced by the ABW with water-to-cement ratio of 0.35. The C/ABW brick may be classified as Engineering Brick Type B due to its high strength and low water absorption property. In the later stage, coarse aggregates were added in the C/ABW bricks design matrix to test the possibility of producing concrete with solidified and stabilized Abrasive Blasting Waste as fine aggregates. The results showed that concrete with ABW has reached compressive strength of 79 MPa at 28th day which is classified as high strength concrete.

Keywords: Abrasive blasting waste, copper slag, solidification and stabilization (S/S), bricks, concrete.

PENILAIAN SISA BAGAS PELELAS LIMBUNGAN YANG DISTABILKAN DAN DIPEJALKAN SEBAGAI BAHAN PEMBINAAN

ABSTRAK

Sejumlah besar sisa bagas pelelas (ABW) telah dihasilkan setiap tahun dari penyingkiran cat lama dari kapal. Pelelas mengandungi logam berat yang dianggap berbahaya oleh kriteria ciri-ciri ketoksikan (TC). Kajian ini menghuraikan suatu penyelesaian berasaskan pemejalan / penstabilan simen (S / S) daripada bagas yang digunakan untuk pembaikan kapal, yang sebahagian besarnya mengandungi sanga tembaga. ABW yang dicampurkan dengan simen Portland Biasa (OPC) yang terdiri daripada nisbah 0-1.5 mengikut berat simen telah diuji untuk pengurasan blok dan kekuatan mampatan. Nisbah air/simen daripada campuran telah ditetapkan pada 0.35-0.5. Keputusan menunjukkan bahawa pengurasan ion logam berat terpilih dari matriks simen adalah rendah dan tidak melebihi Peraturan Garis Panduan daripada United States Environmental Protection Agency (US EPA) dan Jabatan Alam Sekitar, Malaysia berbanding dengan keputusan larut lesap ABW sebelum rawatan S / S. Walau bagaimanapun, penambahan sisa bagas pelelas di dalam simen telah melambatkan proses pemejalan matriks simen tersebut. Kekuatan ABW yang telah dirawat dengan teknik S/S juga pada umumnya lebih rendah daripada adunan simen kawalan. Kekuatan optimum dicapai apabila nisbah C/ABW adalah 1.5 dengan nisbah air/simen 0.35. Di peringkat penyelidikan yang seterusnya, pasir ditambah dalam matriks simen-ABW untuk menghasilkan bata untuk tujuan pembinaan. Kekuatan batu bata C/ABW pada umumnya lebih tinggi daripada batu bata kawalan dan konvensional. Kekuatan optimum yang dicapai apabila 20% berat pasir digantikan oleh ABW dengan nisbah air/simen 0.35. Bata C/ABW boleh diklasifikasikan sebagai Bata Kejuruteraan Jenis B disebabkan oleh kekuatannya yang tinggi dan peratusan penyerapan air yang rendah. Kemudian, agregat kasar ditambah pada rekaan matriks batu bata C/ABW untuk menguji kebarangkalian menghasilkan konkrit dengan sisa bagas pelelas yang telah dipejalkan dan distabilkan. Keputusan daripada ujikaji makmal telah menunjukkan bahawa konkrit dengan ABW telah mencapai kekuatan mampatan 79 MPa pada hari ke 28 yang dikelaskan sebagai konkrit berkekuatan tinggi.

Kata kunci: Sisa bagas pelelas, sanga tembaga, pemejalan dan penstabilan (S/S), batubata, konkrit.

ACKNOWLEDGEMENTS

All praise to Allah. Lord of Universe, The Merciful and The Gracious.

A report of this magnitude could not have been completed without the assistance of numerous individuals. First and foremost, to both my supervisors, Prof. Dr. Ghazaly Shaaban and Prof. Dr. Hilmi Mahmud, two self-dedicated supervisors who help, guide, and give professional comments and suggestions in order to complete this report.

I also would like to express my sincere gratitude to Ms. Kalai and Mr. Yusoff for their continuous assistance in doing the laboratory works.

I also wish to acknowledge my collegues, Ms. Asna and Mr. Jason who always together with me with patience during the preparation and production of this report.

Last but not least, I extend a very special thanks to my husband Ir. Mohd Rashid Ya'acob, beloved family and those who are involved directly or indirectly while finishing this report.

Salmaliza bt Salleh
September 2018

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

ABW	Abrasive blasting waste
ACI	American Concrete Institute
ANSI	American National Standards Institute
APHA	American Public Health Association
ASTM	American Standard of Test Material
BDAT	Best Demonstrated Available Technologies
BET	Brunauer, Emmett and Teller
BS	British Standard
BS EN	British Standard European Norm
C/ABW	Cement to Abrasive Blasting Waste ratio
CaO	Lime
C_3A	Tricalcium aluminate, $3CaOAl_2O_3$
C_4AF	Calcium alumina ferrite, $4CaOAl_2O_3Fe_2O_3$
C_3S	Tricalcium silicate, $3CaOSiO_2$
C_2S	Dicalcium silicate, 2CaOSiO
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
ºC	Degree Celsius
Ck	Coefficient of gradient
CS	Copper slag
d10	Effective size
DOE	Department of Environment, Malaysia
DWT	Dead weight tonnage
FESEM	Field Environment Scanning Electron Microscope

EC	Eurocode
EQA	Environmental Quality Act
EQR	Environmental Quality Report
HSWA	Hazardous and Solid Waste Amendments
ICP-OES	Inductively couple plasma atomic electronic spectrophotometer
kg/m^3	Kilogram per cubic meter
kN	Kilonewton
MOSTI	Ministry of Science, Technology and Innovation
MPa	MegaPascal
OPC	Ordinary Portland cement
%	Percent
Qu	Uniform coefficient
RCRA	Resource Conservation and Recovery Act
RHA	Rice Husk Ash
S/S	Solidification and stabilization
SARA	Superfund Amendments and Reauthorization Act
SEM	Scanning electron microscope
TCLP	Toxicity Characteristic Leaching Procedure
UCS	Ultimate compressive strength
USEPA	United States Environmental Protection Agency
w/c	Water to cement ratio
TBT	Tributyltin

LIST OF APPENDICES

CHAPTER 1: INTRODUCTION

1.1 Research Background

Shipbuilding and repair works contribute to large amount of hazardous waste such as corrosive waste, lead, ignitable waste and chromium.

The production of materials and chemicals in such industrial activities contribute to the increase of hazardous waste magnitude. There is no universal waste treatment or immobilization process that is capable of handling all types of waste produced. A realistic goal, however, is to minimize the risks related to management and ultimate disposal of hazardous waste. Various studies had been carried out to convert hazardous waste such as the industrial sludge into inert substance via several disposal methods such as agricultural land spreading, sea disposal and landfill disposal (La Grega *et al.*, 2010). Cement-based stabilization/solidification (S/S) technology is one of the several treatment technologies for industrial residues and contaminated land. Besides lowering the leaching rate, stabilization/solidification is a technique to reduce the sludge's toxicity and facilitate handling prior to disposal area (Chen et al., 2009).

The processes and techniques of S/S technology have developed into an acceptable and important part of environmental technology. It is a proven technology for the treatment of hazardous wastes and hazardous waste sites (US EPA, 1989) and has been specified by the US EPA (1989) as "best demonstrated available technologies (BDAT)". The goal of S/S technology when applied to waste treatment is to contain the contaminants and prevent their migration into the environment (Wiles, 1988). This is accomplished through the addition of cement and/or additives to transform the waste contaminants into a stabilize form encompassing of mechanical, chemically induced or biological stabilization technique while solidification technique is to ensure the ease of sludge handling, reduce hazard from volatilization, leaching or spillage, and inertness to the environment (US EPA, 1986).

The potential stabilized and solidified sludge will then be explored as a new construction material which will give an added commercial value to the by-product (Malliou, 2006).

1.2 Problem Statement

Abrasive blasting waste (ABW) originating from shipbuilding and repair works is a hazardous material. The metal content and also the chemical substance have harmful effect to the ecological state of the surrounding areas of the shipyard (Chiu *et al.,* 2006). The contaminants will absorb into the soil at shore and also the organisms living in the area. These have harmful effect in fishing and also growth of biotic population in the area. The effluent as a result from ship repair, repainting, repairs and various works done to ships will produce various substances especially wastewater and thus sludge.

One of the most popular blasting media used is copper slag. The possibility of copper slag usage as alternative for concrete aggregate and cement replacement has been studied by various researchers such as Alnuaimi (2012), Brindha *et al*. (2010), Al-Jabri *et. al* (2011), Shi *et al.(*2008), Khanzadi and Behnood (2009) and Moura *et al.* (2007).

However, none of the researches investigate the potential of copper slag after it has been used as an abrasive blasting waste and none of the researches explored the possibility of using the ABW in bricks and concrete.

1.3 Objectives

The main goal of this project is to stabilize the abrasive blasting waste and to explore its use as a new construction material using solidification and stabilization methods. The key objectives of this project are:

i. To characterize the abrasive blasting waste in terms of its physical and chemical characteristics.

ii. To determine the best design mix ratio in order to achieve acceptable compressive strength and leaching limit of solidified and stabilized cement-abrasive blasting waste paste.

iii. To establish the optimum compressive strength of cement-abrasive blasting waste to be applied as construction bricks.

iv. To evaluate feasibility of using abrasive blasting waste as fine aggregates in concrete.

1.4 Scope of Work

Chapter 1 is the introduction of the research work, while Chapter 2 is the literature review, which provides the groundwork for the research study and assessment of techniques that had been used. References from previous literature were taken into consideration to determine the most suitable binding material for stabilization and solidification technique. Chapter 3 elaborates the research methodology that were used in this research. The experimental works are subdivided into four main stages as explained below. The experimental results and discussions are covered in Chapter 4. Chapter 5 presents the conclusions and recommendations derived from Chapter 4.

(a) In stage 1, the scope involved laboratory works for determination of physical and chemical characteristics of the abrasive blasting waste, fine aggregates, coarse aggregates and cement as the selected binding agent. Before the trial mixes are carried out, it is essential to determine the material properties of the abrasive blasting waste as its physical properties and chemical properties will affect the cement mix especially the w/c ratio. Tests results e.g. specific gravity, particle size distribution, porosity, water absorption and chemical contents of the abrasive blasting waste before the stabilization and solidification treatment and other concrete constituents are discussed in Chapter 4.

(b) In stage 2, the laboratory studies involved the mix ratio analysis of the abrasive blasting waste and the binding material in order to achieve an acceptable leaching limit and optimum compressive strength. These two characteristics are the main factors in evaluating the degree of immobilization in the stabilization/ solidification of hazardous waste which is outlined by the UK Waste Disposal Authority (Sollars and Perry, 1989). Cement and water were mixed and prepared as the control paste with various w/c ratio.

Trial mixes between ABW and Ordinary Portland cement were then carried out with ratio ranges from 0.75, 1.00, 1.25 and 1.5 by weight of cement.

(c) Stage 3 consists of the establishment of the engineering properties of abrasive blasting waste-cement as bricks. After the optimum mix in Stage 2 has proven that the abrasive blasting waste is able to be encapsulated with acceptable leaching limit and compressive strength, sand was introduced in the cement paste matrix to produce bricks. 20%, 40%, and 60% of sand weight was replaced by the ABW. Engineering properties of bricks e.g. compressive strength, water absorption and net dry density were tested and the findings were discussed in Chapter 4. The properties of ABW bricks were also compared to control bricks and conventional sand-cement bricks.

(d) Stage 4 covers the development of high strength concrete by incorporating abrasive blasting waste in the design mix. This stage investigates the feasibility of the abrasive blasting waste to be further applied as fine aggregates in increasing the strength of the concrete material.

The activities involved in executing the scope of work are summarized in the flow chart shown in Figure 1.1.

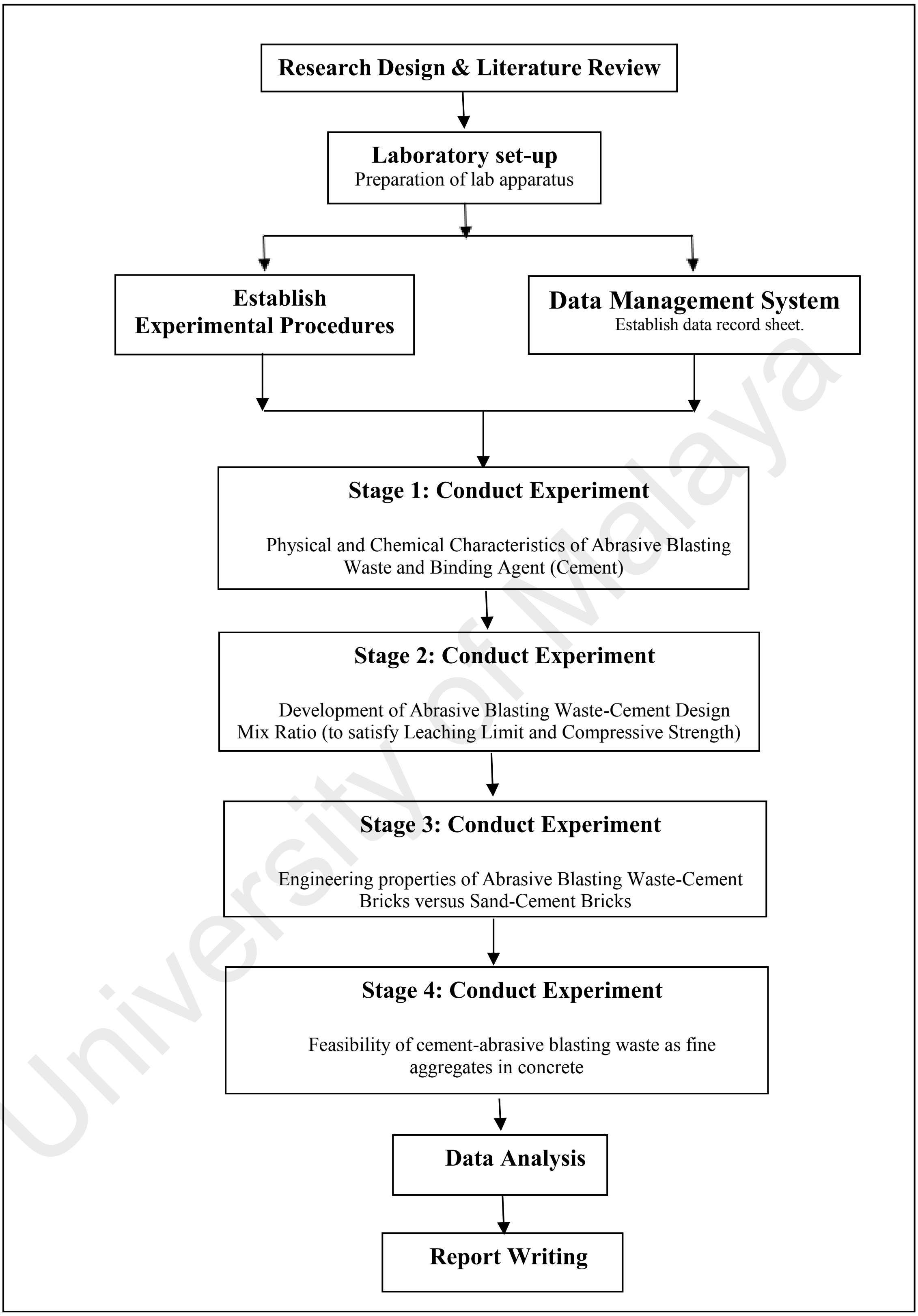

Figure 1.1: Flow Chart of Scope of Work

CHAPTER 2: LITERATURE REVIEW

2.1 Shipbuilding and Repair Industry in Malaysia

In 2011, statistic figures obtained from the Malaysian Association of Ship Owners excluding government agencies show a fleet strength of 589 vessels owned by the members, with a total capacity of about 10 million tonnes deadweight and nearly 7 million gross tonnage. This allows Malaysia to be categorised in the 20 most important maritime nations of the world. In shipbuilding and repair work, activities are also increasing. Malaysia now has 50 boat and ship manufacturing companies. However, only 22 shipyards that have ship repair services. The ship repair and maintenance capacity at Malaysia Shipyard & Engineering (MSE), Johor includes a 140,000 ton and a 400,000 ton dry dock apart from a synchrolift, the largest in the world. Ship repair facilities are also found in Kuching, Labuan, Pulau Pinang, Kuala Terengganu and several other places.

The Government of Malaysia seeks to strengthen the capacity and the capability of the shipbuilding and repair sector under the Third Industrial Master Plan (IMP3) from 2006 to 2020. The push to the shipbuilding and repair sector is amongst the strategic thrusts for the long-term growth and viability of the marine transport sector.

2.2 Abrasive Blasting Waste

Despite the fast-growing of the shipbuilding and repair industry in Malaysia, there has been increasing concern in recent years about pollutants generated by the industry. In particular, abrasive blast media, metals, metal related compound, petroleum associated hydrocarbons and antifouling ingredients in paints have come under scrutiny. One reason for concern with pollutants generated by ship repair activities is the close proximity to water and the potential to pollute this resource. Technical inspections and toxics monitoring of shipyard effluent show that significant levels of pollutants are generated by shipbuilding, repair and maintenance operations.

Vessel maintenance generally involves some amount of abrasive blasting with copper, nickel or some other type of slag, or steel shot. These operations may be carried out on the ship's interior tanks and compartments or on the exterior hull and upper decks. The use of blast abrasive or paint represents a major pollutant source which may be lost, directly or indirectly to the water during the repair work.

Abrasive blasting is generally one of the preliminary tasks performed when a vessel is docked for repairs and maintenance. The task typically involves blasting the vessel hull or upper decks with nickel, copper or some other type of slag or steel – shot to remove layers of old paint. Blasting generates a tremendous volume of spent abrasive which must be cleaned up and contained on a frequent basis.

Abrasive blasting at repair facilities presents an especially challenging task in terms of pollution control. Abrasive blasting clearly is what is known as a "cross media" pollutant which affects air, water, and land. A tremendous amount of spent blast abrasive dust and grit is generated daily.

There are variety of abrasive blast materials that can be used in air or water blasting processes used to remove paint from vessels and marine structures: Blast material particles, also referred to as "grit", are about 1/8" in diameter. These normally jagged, or sharp-edged particles become rounded and reduced in size after being blasted against a vessel's hull, for example, to remove paint and rust.

Vessels, depending on the size, can use an enormous amount of grit for both interior and exterior blasting. One large supertanker, for example, may require up to 40,000 tons of grit just to do interior blasting. The amount of grit needed to remove paint from a vessel's exterior depends on the surface condition of the hull (e.g. was the previous paint put on bare metal, or over existing paint), the nozzle diameter of the hose used in abrasive blasting, and the number of coats to be removed and other contract specifications.

The constituents of abrasive blast vary, but in general the primary components are as shown in Table 2.1.

Table 2.1: Contaminants Associated with Abrasive Blasting in Shipyards

Source	**Potential Contaminants**
Base Material (e.g. steel, aluminum, galvanized steel, copper-nickel and other copper alloys)	Aluminum, cadmium, chromium, copper, iron, lead, manganese, nickel, zinc
Surface Coatings (e.g. primers, anticorrosive and antifouling paints)	Copper, barium, cadmium, chromium, lead, tributyl tin compounds, zinc
Abrasive Blasting Media (e.g. coal slag, copper slag, nickel slag, glass, steel grit, garnet, silica sand)	Arsenic, beryllium, amorphous silica, cadmium, cobalt, lead, manganese, nickel, silver, vanadium

(US EPA, 2000)

One of the most popular blasting media used is the copper slag. The possibility of copper slag usage as alternative for concrete aggregate and cement replacement has been studied by various researchers such as Sharma and Khan (2017), Nazer *et. al* (2016), Alnuaimi (2012), Brindha *et al.* (2010), Al-Jabri *et. al* (2011), Shi *et al.* (2008), Khanzadi and Behnood (2009) and Tixier (1996). In brief, replacement of the coarse fraction of natural aggregate by copper slag of equivalent size distribution was slightly decreased the compressive strength of concrete and retard the hardening process of concrete. In the case of replacement of the fine aggregates, CS increased the compressive strength of the concrete up to certain percentage of replacement (Brindha and Nagan, 2011) and the presence of sulfates caused durability problems (Tixier, 1996). Few commercial uses of copper slag as replacement of Portland cement in concrete also have been reported (Gorai *et al.,* 2005). Table 2.2 summarize recent researches done on copper slag.

Table 2.2: Previous Research Findings on Copper Slag

Author	**Nature of Study**
Sharma and Khan (2017)	The research is aimed to investigate the sustainable utilisation of Copper Slag (CS) as fine aggregates in Self Compacting Concrete (SCC) using fly ash (FA) and silica fume (SF) as Supplementary Cementitious Materials. The fresh properties of SCC mixes were found to be escalating up to 100% CS substitution. The maximum improvements in compressive and splitting tensile strength with respect to control were obtained as 20% and 60% CS substitution.
Geetha and Madhavan (2017)	This paper is focused on developing a corrosion resistant concrete using copper slag, fly ash and silica fume with Portland cement for use in marine environments. A compressive strength of 70 MPa and flexural strength of 6 MPa was achieved with copper slag and fly ash.

Table 2.2 continued

Author	**Nature of Study**
Nazer *et. al* (2016)	In this paper, the copper slag abandoned in landfills is proposed as a new building material. Copper slag-Portland cement mortars with the substitution of 25% (by weight) of cement by copper slag and alkali-activated slag mortars cured at 20 and 65 °C were made, to determine the compressive strength. The results indicate that CS has good binding properties.
Brindha *et. al* (2011)	The research was on the decomposition and stability of concrete consist of CS as a partial alternative for fine sand and cement. The result indicates that the compressive strength and the tensile strength of the CS is greater to the corresponding control concrete. Copper slag also shows good stability features and it has concluded that it can be use as replacement to fine sand.
Al- Jabri et. al (2011)	Examination was done on the impact of using CS as fine aggregate on the properties of cement mortars and concrete. The range of proportion of CS ranging between 0 to 100 % as fine aggregates as an alternative in mortars and concrete mixtures were prepared. The properties examined were strength, workability, and stability of the mortars and concrete. The result indicates that the mixtures produced comparable or greater compressive strength than strength of control mixture. The workability also improves considerably with additional of CS.

Table 2.2 continued

Author	Nature of Study
Khanzadi et. al (2009)	The study was to examine the possibility of CS as a coarse aggregate in high-strength concrete. The assessment on the compressive strength, splitting tensile strength and spring back hammer of the high strength concrete was made between limestone aggregate and CS aggregate. As a result, the CS aggregates shows 10-15% increment in the compressive strength and 10-18% increment in the splitting tensile strength.
Shi et. al (2008)	The study on CS features and its impacts on the engineering properties of cement, mortars and concrete. As the result, when CS used as cement or an aggregate alternative, the cement, mortar and concrete have good performance and developed higher strength than normal ordinary Portland cement.

Spent abrasive blast material may contain a variety of pollutants. Fresh, or unused abrasive blast media is even considered a “dangerous” or “special” waste due to gill abrasion which can be fatal to some fish: therefore, abrasive blast media, used or unused, should not be discharged into the waters.

When hydroblasting, rust inhibitors such as sodium nitrite or diamonium phosphate may be used. Antifouling paints are used on vessels and marine structures to control the growth and attachment of “fouling”, organisms such as barnacles, seaweed and algae. This is the intended effect of antifouling ingredients in paint. However, some antifouling ingredients, such as Tributyltin (TBT) can have a deadly effect on species other than fouling organisms. TBT is highly toxic in small concentrations to fish, oysters, clams and other forms of water life, hence proper management of TBT-containing paint, and while blasting vessels that have been painted with TBT paint, is extremely important.

The most common ways TBT and other antifoulants get into the environment are external blasting out of dry docks or contained areas, uncovered or loosely covered sandblast waste piles where grit blows away, or rainwater leaches antifoulant into nearby surface water or groundwater, sweeping or hosing sandblast grit waste into water, and overspray of TBT or other antifouling paints.

Under the Department of Environment Malaysia (1989), the abrasive blasting waste is categorized as one of the hazardous waste and classified as “schedule waste” code SW 104 which described as “dust, slag, dross or ash containing arsenic, mercury, lead, cadmium, chromium, nickel, copper, vanadium, beryllium, antimony, tellurium, thallium or selenium excluding slag from iron and steel factory”.

Based on the notification on scheduled wastes received by Department of Environment (DOE), a total of 2,918,478.34 metric tonnes of scheduled wastes were generated in Malaysia in 2015 as compared to 2,541,762.34 metric tonnes in 2014, which shows an increasing trend of 14.82%. In 2015, it was found that dross, slag, clinker, ash, heavy metal sludge, gypsum, e-waste and mineral sludge were the main categories of waste produced in the country. Table 2.3 gives the quantity of scheduled waste SW104 generated in year 2015 (DOE, 2015).

Table 2.3: Quantity of Scheduled Waste Generated by Malaysia Industry in 2015

No	Name of Waste	Waste Code	Quantity of Waste	
			(MT/Year)	Percentage (%)
1	Dross / slag / clinker / ash	SW 104	1,062,259.39	36.40
2	Heavy metal sludges	SW 204	846,680.03	29.01
3	Gypsum	SW 205	548,768.49	18.80
4	Mixture of scheduled waste & non-scheduled waste	SW 422	49,482.15	1.70
5	Spent lubricating oil	SW 305	49,280.71	1.69
6	E-waste	SW 110	47,962.73	1.64
7	Spent acids	SW 206	43,735.85	1.50
8	Used container	SW 409	28,207.57	0.97
9	Waste of inks & paints	SW 417	26,602.07	0.91
10-77	Others		215,499.35	7.38
Total			**2,918,478.34**	**100.00**

(Adapted from DOE Malaysia Environmental Quality Report 2015)

2.3 Toxic and Hazardous Waste

Toxic and hazardous waste may refer to all non-product toxic and hazardous or effluents (solid, semisolid, liquid and gaseous) from industries into all environmental media – atmosphere (both inner and outer), water and soil. Various terms are used to describe toxic and hazardous waste. It is referred as “scheduled waste” in Malaysia, “Chemical waste” in Denmark, “special waste” in the United Kingdom, “toxic and hazardous” in Italy and France and “problem waste” in Finland.

There is no universally accepted definition of toxic and hazardous waste. However, there are similarities in the definition used by researchers, international organizations and various countries. For example, US EPA (2005) defined hazardous waste as a waste with a chemical composition or other properties that makes it capable of causing illness, death, or some other harm to humans and other life forms when mismanaged or released into the environment. Department of Environment and Energy, Australia defines hazardous waste as waste prescribed by the Hazardous Waste (Regulation of Exports and Imports) Act 1989, where the waste has any of the characteristics mentioned in Annex III to the Basel Convention. These characteristics include explosive, flammable liquids/solids, poisonous, toxic, ecotoxic and infectious substances. DOE (2005) defines scheduled wastes as substances that are highly flammable, corrosive toxic and easily react or cause explosion when mixed with other substances. They may exist in a liquid, solid or semi-solid form. The accumulation and accelerating output of these toxic and hazardous wastes will lead to environmental degradation and irreversible damage to the ecosystem. In Malaysia, toxic and hazardous waste are defined by a list of 107 categories of waste listed in the DOE First Schedule of the Environmental Quality (Scheduled Wastes) Regulations 1989.

2.3.1 Types of Hazardous Waste

Hazardous waste can be grouped into several types (Palmark, 1985):

a) Recoverable wastes: The primary hazardous waste type that can be treated in recovery plants are contaminated organic solvents or metal containing wastes.

Sometimes it is also possible to recover waste oil and transformer oil containing PCB.

b) Burnable Waste: Practically all hazardous wastes with the exception of inorganic wastes and explosives can be regarded as combustibles.

c) Toxic wastes that can be detoxified: Toxic waste that can be detoxified include inorganic and organic wastes. Examples of inorganic wastes that can be detoxified by chemical methods are the cyanide and chromate containing wastes originating from the metal plating industry. On the other hand organic waste includes pesticides containing chlorine that can be destroyed by a dechlorination process.

d) Waste containing heavy metals in association with acids or alkalis: These wastes may originate from acid pickling baths, electroplating baths, corrosive baths or sludge from electroplating industries. Heavy metals commonly found in these wastes are Fe, Cr, Ni, Cu, Zn, and Cd. Acids typically associated with these wastes are sulfuric acid, hydrochloric acid and alkalis such as sodium hydroxide.

e) Hazardous wastes that cannot be treated by simple incineration or detoxification. Examples include mercury containing batteries, explosives or cylinders containing pressurized gases.

f) Waste that can be landfilled: Waste that can be landfilled are hazardous waste products that are solid compounds originating from processing of hazardous wastes, or for which no process exist which render them more harmless.

2.4 Hazardous Waste Generation in Malaysia

Even though toxic and hazardous wastes are generated in agriculture, mining, hospitals, research laboratories and households, the primary source of toxic and hazardous waste is the industrial sector.

In Malaysia the source of each category of scheduled waste is described in terms of either the type of industry or process that generates the waste. Toxic and hazardous wastes in Malaysia originate from three (3) major sources i.e. industrial, agricultural and domestic sources. Toxic and hazardous waste from the industrial sector arises from effluent discharges, emissions, and solid waste, while wastes from agricultural sector arises from the direct application of pesticides and herbicides for crop protection and animal production.

Studies conducted by Dames and Moore, a U.S. engineering consulting firm indicated that approximately 380,000 cubic metres of scheduled waste were generated by industries in Malaysia in 1987 (Dames and Moore. 1987). This figure however does not include waste from palm oil, rubber and mining industries. The waste come from various forms and compositions. Sludge with heavy metals made up about 15% of the total waste while the metal finishing industries contributed to about 30% of the total waste produced. A survey conducted by the Department of Environment, Malaysia showed that approximately 630,000 metric tonnes of scheduled waste were produced in 1996. Dross/slag/clinker accounts for approximately 50% of the total waste. Comparing this the 1987 figure, dross/slag/clinker contributed to only 7.06% while mineral sludge, heavy metal sludge accounted approximately 15% and 11% respectively. While in 2015, a total of 2,918,478.34 metric tonnes of scheduled wastes were generated. Of the total waste generated, dross/slag/clinker/ash, heavy metal sludge, and gypsum were the main categories. By comparing the production of scheduled waste in year 1996 and 2015, steep increase of 1,658,478.34 metric tonnes were detected.

From the 2015 Malaysia Environmental Quality Report, a total of 452,956.76 metric tonnes (15.52%) of waste were being recovered locally and abroad. This showed a decrease of 30.26% as compared to 649,496.69 metric tonnes in 2014. From the total, 446,077.76 metric tonnes (15.28%) of scheduled wastes were recovered at local off-site facilities and 6,879.00 metric tonnes (0.24%) were exported for recovery at foreign facilities abroad (DOE, 2015).

A total of 165,028.05 metric tonnes (5.65%) of waste were treated and disposed for final disposal, at Kualiti Alam Sdn. Bhd. (120,221.72 MT), Trienekens (Sarawak) Sdn. Bhd. (19,283.00 MT) and 25,523.32 metric tonnes (0.87%) of clinical wastes were incinerated at licensed off-site facilities. The amount showed an increase of 5.28% from a total of 156,750.89 metric tonnes of scheduled waste disposed in 2014. A sum of 445,867.97 metric tonnes (15.28%) of scheduled waste were treated on-site; while 299,622.49 metric tonnes (10.27%) were stored on-site at waste generators' premises. Two (2) land farms and fifteen (15) on-site waste incinerators has been licensed by DOE to allow for on-site treatment and incineration respectively.

Of the total wastes produced in 2015, 1,555,003.07 metric tonnes (53.24%) were granted conditional approval to be managed under special management as stipulated under Regulation 7, Environmental Quality (Scheduled Wastes) Regulations, 2005 (DOE, 2005). The amount represented an increase of 77.43% as compared to 876,415.44 metric tonnes in 2014. These waste streams are mostly generated from coal-fired power plant (44.71%), sludges from drinking water treatment facilities (41.51%) and others (13.78%).

2.4.1 Legislation Governing Toxic and Hazardous Waste in Malaysia

Policy objectives on hazardous waste management in Malaysia are reflected in three regulations on scheduled wastes. The Environmental Quality (Scheduled Wastes) Regulations 1989, Environmental Quality (Prescribed Premises) (Scheduled Wastes Treatment and Disposal Facilities) Order 1989 and Environmental Quality (Prescribed Premises) (Scheduled Wastes Treatment and Disposal Facilities) Regulation 1989 were gazette on April 27, 1989 and brought into enforcement on May 1, 1989 under the Provisions of the Environmental Quality Act (1974) (EQA and Regulations, 1997). The provisions of the legislation are comprehensive including requirements for management of the generation of scheduled wastes from all industries, large and small-scale industries in both public and private sectors. Specifically, the Environmental Quality (Scheduled Wastes) Regulations 1989 govern the behaviors of the wastes generators as well as the person ("contractor") undertaking off-site handling, transport or storage of hazardous wastes so scheduled.

Scheduled waste falls within 107 categories of waste listed in the First Schedule of the Environmental Quality (Scheduled Waste) Regulation 1989. The scheduled wastes identified are organic wastes, inorganic wastes, pathological wastes and waste mixtures. Radioactive wastes are excluded from the list of scheduled waste.

Environmental Quality (Prescribed Premises) (Scheduled Wastes Treatment and Disposal Facilities) Order 1989 prescribed six types of premises whereby their occupation and use require written permission and license from the Department of Environment. The Environmental Quality (Prescribed Premises) (Scheduled Wastes Treatment and Disposal Facilities) Regulations 1989 however provides procedures for license application, renewal and ownership transfer. It also states the requirement for record keeping and submission of an inventory of scheduled wastes received, stored, treated, recovered, destroyed, disposed of or otherwise handled at the prescribed premises to the Department of Environment.

2.4.2 Hazardous Waste Management in Malaysia

In Malaysia, before the existence of the scheduled waste treatment and disposal facility, industries were forced to store schedules waste (mostly in the form of filter pressed sludge) in their premises over many years as there was no final treatment/disposal route for them. These stored wastes took up much factory spaces as well as posing significant danger to the public and environment. Some industries however, do obtain a license to dispose the stabilized waste at sanitary landfills. There are many refuse disposal sites all over the country that also cater for industrial waste disposal. However, none of them is suitable for the disposal of toxic and hazardous waste. Additionally, illegal dumping of such waste does take place resulting in a significant impact to the environment and general public.

Studies conducted by Dames and Moore (1987) showed that scheduled wastes are being disposed of in the following manner:

i. Open burning
ii. Dumping in drains of surface ground
iii. Dumped off-site at a dumping ground
iv. Taken outside the country for recovery or treatment
v. Dumped in factory's premises
vi. Reclaimed
vii. Sold (for the purpose of reclamation)
viii. Stored in the factory's premise waiting for disposal or treatment options.

With the incorporation of Kualiti Alam on 9th December 1990, the first integrated scheduled wastes treatment facility in Malaysia, the stabilized sludge or liquid wastes can be sent to Kualiti Alam for treatment and final disposal. The presence of the scheduled wastes treatment facility provides an option for the treatment and disposal of hazardous waste generated by the industries in Malaysia.

From the Malaysia Environmental Quality Report 2015, the scheduled wastes which were sent to the licensed premises (Kualiti Alam Sdn Bhd and Trienekens (Sarawak) Sdn Bhd for final disposal are sludge containing one or several heavy metals, mixed wastes, dust / slag / dross or ash containing arsenic / mercury and spent inorganic acid. Such wastes were either incinerated, treated physically and chemically, solidified or disposed in secured landfill depending on their characteristics. As shown in Figure 2.1, most wastes sent to Kualiti Alam Sdn Bhd and Trienekens Sdn Bhd were landfilled (54.8%), followed by incinerated (34.6%), solidified (7.7%) and treated physically and chemically (2.9%) (DOE 2015).

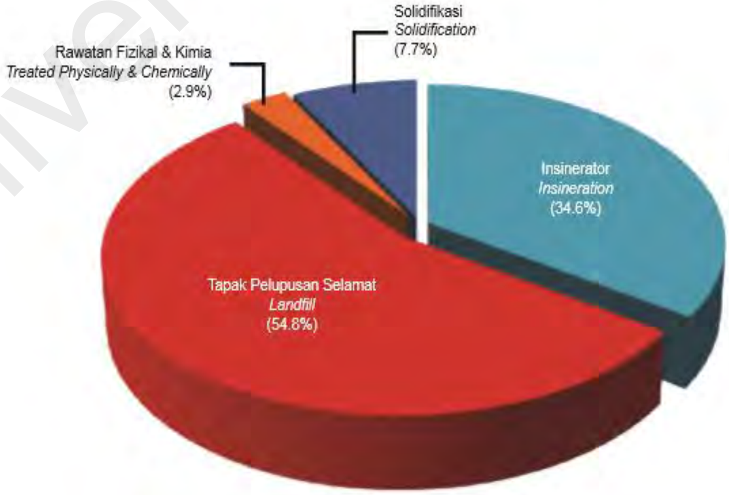

Figure 2.1: The Type of Treatment and Disposal of Scheduled Wastes (Adapted from Malaysia EQR, DOE 2015)

2.4.3 Provision for Delisting – Improvement to Existing Law

Whilst presented scheduled waste regulations are seen as comprehensive, additional provisions to these laws should be viewed as improvements opportunities as the country progresses toward being an industrialized nation. An aspect, which is absent in the existing laws to be highlighted in this section, is regarding delisting of waste.

Delisting in general term means a party, be it an individual or an organization, may seek to exclude a waste, at a particular generating facility by demonstrating to satisfaction of the Department of Environment that is does not meet any of the criteria under which the waste was listed as hazardous. This particular provision should be advocated to the DOE and in turn relevant governmental bodies and industrial forums can initiate detailed procedures for waste delisting.

A good reference to such initiative is in the United States, whereby the Environmental Protection Agency (US EPA) has instituted delisting provisions apart from others regulations governing environment conservations. In brief, a party initiates delisting through submission of a petition to delist the waste. In turn, the US EPA provides a mechanism for technical evaluation of the petition as well as public review and comment. After the US EPA completes its review, a notice will be published in the Federal Register, and this is expected within 6 – 9 months. A public meeting will be held to discuss the delisting petition prior to the US EPA making a final decision.

Currently, the US EPA is running a project with Michigan Department of Environment Quality to find ways to streamline delisting regulations in order to make the process less time consuming. To substantiate the value of these efforts, the US EPA has issued a preliminary report that highlighted that the delisting of hazardous wastes has resulted in waste treatment net savings of US$1.7 billion and US$2.38 billion in disposal savings.

In conclusion, delisting of waste should be introduced into the existing environmental laws in Malaysia. Small- and medium-scale industries that are constrained with financial resource, may gain benefit from this delisting provision through more economical options other than disposal and treatment at Kualiti Alam.

Such alternatives include one-site waste treatment via a stabilization/solidification process.

2.5 Treatment Technologies

The main objectives of hazardous waste treatment irrespective of the method are to improve the handling and physical characteristics of the waste, to decrease the surface area across which the pollutants can transfer or leach, to limit the solubility of any hazardous constituents contained in the waste, and to detoxify the hazardous constituents (US EPA, 1982).

Various treatment alternatives are available once toxic and hazardous waste are generated. In general, the treatment processes aim for volume reduction, component separation, detoxification, destruction, storage and material recovery. The treatment technology can be classified as physical, chemical, biological, thermal and immobilization. The choice of treatment and disposal methods depends upon several factors such as waste composition, form or state of the waste, relative treatment cost and government regulations.

2.5.1 Stabilization/Solidification Technology

The terms “stabilization” and “solidification” refer to treatment processes designed to immobilize, isolate or contain hazardous industrial waste material. Basically the technology involves the transformation of a hazardous waste into a waste form suitable for long-term disposal.

Stabilization/ solidification (S/S) technology is widely acceptable because besides lowering the leaching rate, the technique reduces the sludge's toxicity and facilitates handling prior to disposal area (Chen et al., 2009). These two terms are used interchangeably to describe the immobilization of hazardous constituents. The distinction between the two terminologies are:

Stabilization: A process of converting a hazardous waste to a physically and chemically more stable form (Chen et al., 2009).

Solidification: converts liquid waste, semi-solid sludge or a powder into a massive, solid, and uniform material that will allow easy handling and transportation to disposal sites (Chen et al., 2009).

The objectives of stabilization/solidification are to achieve and maintain the desired physical properties and chemically stabilize or permanently bind contaminants.

Other terms frequently used in the discussion of S/S technology include chemical fixation, microencapsulation and macroencapsulation. Chemical fixation implies the transformation of toxic contaminants to a non-toxic form material with an impermeable, chemically inert material between the waste material and the environment while microencapsulation and macroencapsulation is the encapsulation of individual particles and encapsulation of an agglomeration of waste particles respectively. The treatment protects human health and the environment by immobilizing contaminants within the treated material. Immobilization within the treated material prevents migration of the contaminants to human, animal and plant receptors.

S/S treatment has been used to treat radioactive wastes since the 1950s and hazardous waste since the 1970's (Wilk, 2007). The historical development of the S/S technology was extensively presented by Conner and Hoeffner (1998). The origin of the present day S/S technology has its roots in four main areas of the technology that were practiced prior to 1970. These include the solidification of radioactive waste in drums for transportation, the treatment of mine tailings to be used as backfill, the use of fly ash-lime mixtures as a base for road construction and the use of sodium silicate with setting agents, cement and organic polymerization for grouting and soil stabilization.

Generally, the goal of stabilization/solidification process is the safe, ultimate disposal of hazardous waste through landfilling or some other productive use. Ideally, the objective is to completely transform the potentially toxic contaminants into non-toxic form. The optimum S/S process should have the following characteristics (Thompson *et al.,* 1979):

- The physical placement of the final product should not render the land on which it is disposed of unusable for other purposes.
- It should also result in the formation of an impervious mass, with good dimensional stability and load bearing characteristics and wet-dry and freeze-thaw weathering resistance.
- It should employ combinations of industrial waste products.
- The technology applied should be economical.

However, no S/S process has been developed that is optional or applicable to every type of hazardous industrial waste. The advantages and disadvantages of S/S processes are affected by the type of process, the waste, the condition of the site and other specific factors. For example, the use of pozzolan cementation type of reactions are relatively inexpensive and easy to handle. This process however will increase the total volume of the final product. On the other hand use of a polymeric system results in a small volume increase and sometimes improved product performance. However, the cost and the difficulty in handling the process are factors to consider. Hence, specific conditions must be carefully considered when comparing the advantages and disadvantages of any S/S process.

U.S. Environmental Protection Agency (US EPA) have consider that S/S as an established treatment technology. The hazardous wastes are regulated in the United States under the Resource Conservation and Recovery Act (RCRA). These wastes are grouped into two classes: RCRA-listed and RCRA-characteristic. Listed hazardous wastes are wastes produced by industry that are generally known by the US EPA to be hazardous. Treating, storing, and disposing of listed waste according to RCRA hazardous waste management regulations. These wastes are treated in order to reduce hazard potentials after land disposal. S/S technology can be used to eliminate these hazardous characteristic. S/S has been identified as the Best Demonstrated Available Treatment treating a variety of difficult to manage waste materials for reuse or disposal (US EPA, 1993).

S/S treatment is used during remediation of contaminated properties to treat contaminated media. In United States, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) are conducting the best known and documented remediation. CERCLA program used to remediate abandoned or uncontrolled properties where hazardous substances have been released and pose an endangerment to human health and environment. The program is funded by a tax known as “Superfund” program that collected from petroleum and chemical manufacturer that cause the contaminant. At the Superfund program remediation sites, S/S is the mostly selected treatment technology for controlling the sources of environmental contamination

(US EPA, 2001). Figure 2.2 shows the frequency of S/S treatment used compared to other technologies at U.S. Superfund sites where sources of contamination have been addressed.

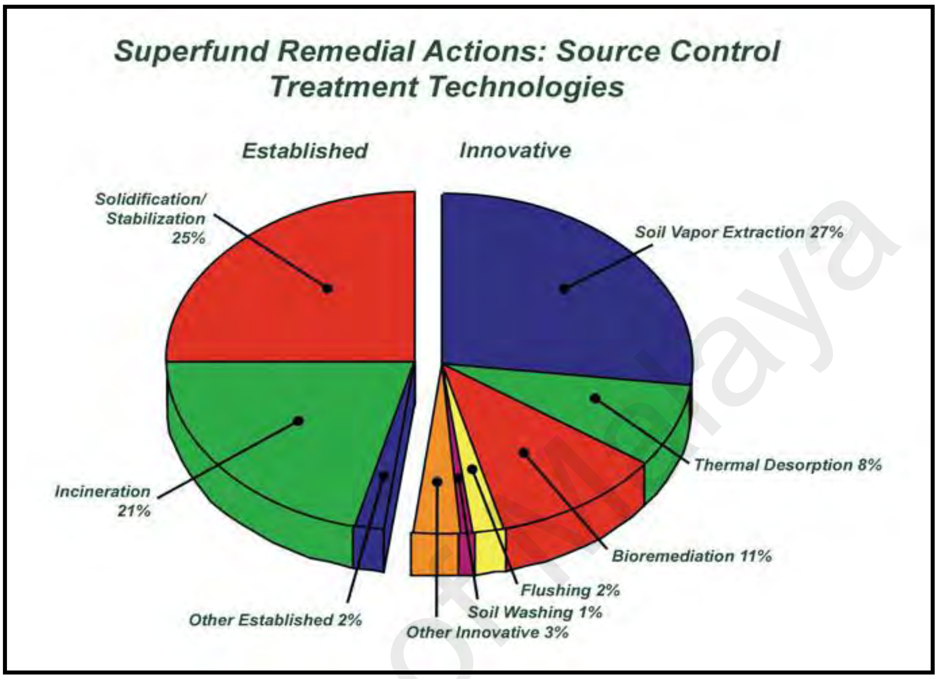

Figure 2.2 Frequency of S/S Treatment Used Compared to other Technologies at U.S. Superfund Sites (Adapted from Wilk, 2007)

In short, S/S processes have been applied to a wide variety of wastes, both hazardous and non-hazardous, nuclear and nonnuclear, inorganic and organic, liquid and solid (US EPA, 1993). Therefore, S/S treatment system can reduce contaminant mobility and can treat contaminated soil or sludge in-situ or ex-situ.

2.5.2 Position of S/S in the U.S. Environment Protection Agency (USEPA) Environmental Management Options Hierarchy

The USEPA's hierarchy of hazardous waste management is shown in Figure 2.3. The hierarchy lists, in descending order of emphasis, technical alternatives for the management of hazardous waste. Pollution prevention and waste minimization programs should be instituted to reduce the volume of waste at the source or to recover, reuse or recycle the waste. If the waste cannot be eliminated or reduced, destructive treatment methods should then be examined. For degradable contaminants, treatment technologies that destroy the contaminant are preferred (US EPA, 1993).

First Choice (Pollution Prevention):

Reduce (Eliminate Waste Product at the Source)
- Design Long-lived, Low-Impact Product
- Use Less Hazardous Input Material
- Minimize Use of Non-Recoverable Input Material and of Water
- Conserve Energy Technology and Practices

Second Choice (Pollutant Prevention):

Reuse (Closed-Loop Recycling)
- Recover Chemical
- Reuse Water
- Recover Waste Material

Third Choice:

Recycle Off-Site
- Ensure Safe Transport to Recycling Operation
- Select Environmentally-Sound Recycling Technology

Fourth Choice:

Threat and Dispose of Unavoidable Waste Safely
- Minimize Volume and Toxicity of Wastes
- Dispose of Safely

Figure 2.3: US EPA Hierarchy of Hazardous Waste Management (Adapted from US EPA Technical Resources Document, 1993)

2.5.2.1 Regulatory Considerations

This section is intended to provide a brief introduction to the major regulatory considerations for S/S. It is very important for anyone considering the use of S/S treatment to consult the regulatory agencies that have authority over that waste. Clean up and disposal of hazardous wastes are regulated primarily by two federal laws and their amendments. First are the Resource Conservation and Recovery Act of 1976 (RCRA), as amended by the Hazardous and Solid Waste Amendments of 1984 (HSWA). These give US EPA authority to regulate disposal of hazardous waste and set standards for treatment (US EPA, 1993).

The second major law regulating hazardous waste is the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) of 1980, as amended by the Superfund Amendments and Reauthorization Act (SARA) of 1986. CERCLA regulates the clean-up of spilled materials and abandoned hazardous waste sites (US EPA, 1993).

Remedial sections may present technically complex problems that are expensive to resolve. The selection of technical measure take place only after a full evaluation of all feasible alternatives based upon economic, engineering, environmental, public health, and institutional considerations (US EPA, 1986).

2.5.2.2 Other Environmental Regulations

In addition to RCRA, CERCLA and Environmental Quality Act (EQA), other Malaysia Government body and environmental legislation may be applicable to the use of S/S are:

a. Department of Environment (DOE) Malaysia
b. Ministry of Science, Technology and Innovation (MOSTI)
c. Merchant Shipping Oil Pollution Act
d. Toxic and Hazardous Waste Regulation (B.C. Reg. 63/88)

2.5.3 Classification of Waste Stabilization/Solidification Technology

Stabilization/solidification process are often classified based on the principal additives used to obtain the solid waste form. In general the processes can be classified based on inorganic and organic fixation (Sollars and Perry, 1989). A general classification of S/S process is presented in Figure 2.4.

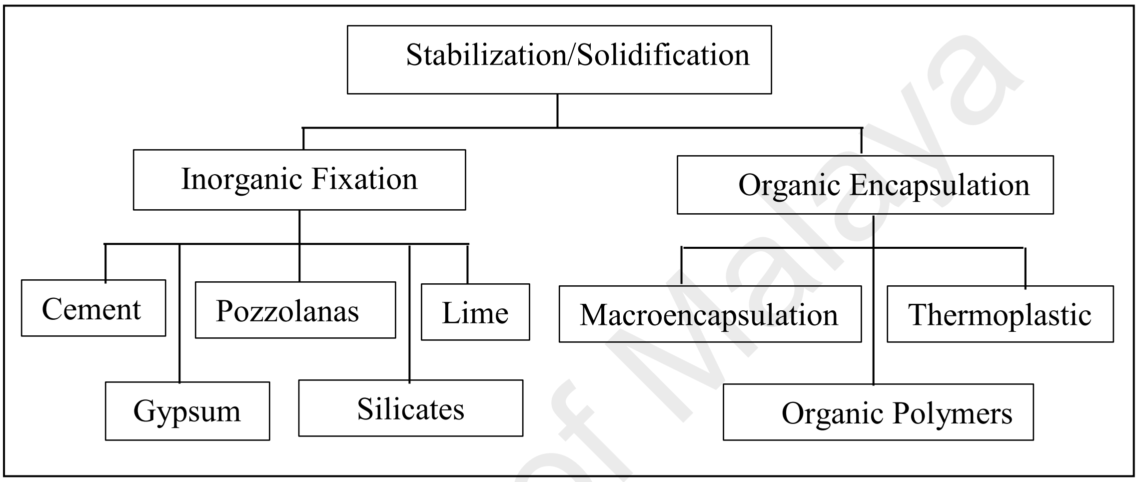

Figure 2.4: Classification of Stabilization/Solidification Technology

Processes based on inorganic additives use hydraulic cements, pozzolanas, lime, gypsum, and soluble silicates. Portland cement is commonly used; other types of cements used include aluminous cement, slag cement, etc. Organic stabilization/solidification with thermoplastic binders and organic polymerization has been applied to selected hazardous waste and is on a much smaller scale compared to stabilization/solidification with cement and pozzolanas (Barth, 1990).

Organic-based processes are hydrophilic and are thus suited for organic waste streams such as hydrocarbon or pesticides. The resultant waste forms normally show low contaminant leachability due to the impervious matrices formed. There is usually no reaction between the waste constituents and the polymer; hence the long term stability of the waste forms depend entirely on the physical integrity of the waste forms.

2.5.3.1 Applicability of Cement-Based Processes as Binder to Waste Treatment

Waste characteristics are among the important factors affecting waste stabilization. Not all wastes can be subjected to cement-based processes. The presence of small quantity of certain compounds can reduce the strength and containment characteristics of binder-waste mixes used in the process. Some compounds act as accelerators while others act as retarders.

Wastes that can be effectively stabilized/solidified are mainly inorganic materials in aqueous solutions or suspension containing substantial amount of toxic heavy metals and /or inorganic salts. In the United States wastes which are most commonly considered for solidification or/and stabilization are those designated hazardous by the US EPA and produced in large amounts (US EPA, 1982b). Most hazardous inorganic industrial wastes pose a hazard due to the high concentrations of toxic metals. Even though they are present in the form of insoluble hydroxides or sulphides, changes in the pH or oxidation conditions once they have been introduce into the environment can result in their mobilization.

The conventional cement-based process are designed to bind complex soluble metal ions present in an inorganic waste stream by first neutralizing the waste to precipitate them as insoluble metal hydroxides. In S/S terms, the mixture of these cement bond wastes are identify as ‘paste’ (Pan *et. al*, 2015, Bhatty and West, 1996 and La Grega *et. al* 1989).

Unfortunately, the conventional processes are generally unsuitable for the treatment of waste containing organic compounds due to the interfering effects of organics on various hydration products. Generally organic compounds are poorly retained and have a detrimental effect on the cement matrix (Tittlebaum, et al., 1985; Jones, 1990; Montgonmery et al., 1991). Even though it is known that organics can alter the setting characteristics of Portland cement, it is unclear at what concentrations the organics will interfere with the setting reaction and alter the cement matrix (Ramachandran, 1976; Cullinane, et al., 1986; Pollard, et al., 1991).

Inorganic wastes with greater than 10 to 20 percent organic constituents are generally not recommended for treatment by currently available S/S process as the organics interfere with the chemical processes that are important in binding the waste material together (US EPA, 1982a). Organic wastes are normally treated by destructive methods such as incineration, UV-ozone or biological systems. These treatments when properly employed produced mainly CO_2 and H_2O. However, complete detoxification of organics and organic-metal waste by chemical, biological and incineration are not always possible. Even though incineration is the best way to dispose of volatile organic waste, the presence of heavy metals and the high operating cost as well as the low calorific value of the waste renders it inappropriate for treatment of such waste (Vipulanandan and Krishnan, 1990).

2.6 Binder

The treatment of abrasive blasting waste using binding material is a cost effective technique that does not use large sum of investment for a dedicated facilities. The binding process involve addition of treated or untreated waste with a mixture of binding solution that normally consist of several types of substance to aid in the process (Silva, 2007). Cement is the most adaptable binder currently available for the immobilization of hazardous sludge (Chen et al., 2009).

Ordinary Portland Cement (OPC) is the most commonly used binder at construction sites for making mortar and concrete. It binds the grains of sand together when water is added and the setting and hardening process are completed. Used on its own, cement is too sticky, set too hard and would develop severe shrinkage cracks. It is therefore always diluted with 3, 4 or 6 equal volume of sand. The setting and early part of the hardening processes of Portland cement involve complicated chemical reactions between the mixing water and the cement powder in a batch of mortar or concrete. These reactions need to take place in damp conditions called ‘curing’ for full hydration process which usually takes duration of 28 days. Cement is the product obtained by pulverizing clinker formed by calcine raw materials primarily consisting of 60-65% of lime (CaO), 20-25% of silicate (SiO_2), 4-8% of alumina (Al_2O_3), and 2-4% of iron oxide (Fe_2O_3) (Gambhir, 2005).

Besides acting as a great binder, cement–based processes, are the most suitable S/S method for aqueous waste streams since water is needed for the hydration of cement. The process utilizes a mixture of Portland cement and sludge along with certain other additives (some proprietary) such as fly ash to produce a monolithic, rock like mass for disposal. Since cement-based processes create an alkaline environment, they are particularly effective for wastes containing toxic metals such as incinerator-generated wastes, metal-finishing wastes, inorganic sludge from electroplating and others. The high pH of the cement is suitable for the containment of the metals in their insoluble hydroxides or carbonate salts.

Cement-based processes have been well documented and several vendors have published a list of waste streams treated with cement-based processes (Pojasek, 1978; US EPA, 1989). Waste streams commonly treated are aqueous inorganic waste streams or suspensions that contain toxic heavy metals and/or inorganic salts. The waste is normally pretreated to reduce the mobility of contaminants (oxidation or reduction, precipitation) or to reduce its volume (dewatering). Wet wastes or sludge are mixed directly with the cement and other additives, to initially form a colloidal calcium-silicate-hydrate gel of indefinite composition and structure. The hardening of cement is brought about by the interlacing of thin, densely-packed, silicate fibrils incorporated the added aggregates and / or waste into a monolithic, rock-like mass.

2.6.1 Hydraulic Cement and Pozzolanic Additive

Alkaline matrices such as Portland cement and lime are commonly used in S/S of waste. Their alkalinity reduces the solubility of much inorganic toxic and hazardous wastes as well as inhibiting microbiological attack. Additional, since these matrices require water for their reaction, they could readily incorporate wet sludge. Mineral admixtures or pozzolanic materials such as fly ash (Lange, et al., 1997; Akhter, et al., 1997; Cheeseman, 1994; Cote, 1986; Hills, 1992), and blast furnace slag (Macias, et al., 1997) have been used in cement-based waste treatment and has been extensively reviewed by Conner and Hoeffner (1998).

2.6.1.1 Ordinary Portland Cement

Cement is a material with adhesive and cohesive properties that enable it to bond mineral fragments into a compact whole (Neville, 1995). It can be described as a finely powdered, calcareous material, that when mixed with water, forms a plastic paste that sets and eventually hardens to rock-like consistency with water (Double and Hellawell, 1977).

Ordinary Portland cement, produced by the calcination of limestone and clay (Neville and Brooks, 1987) is the most commonly used hydraulic binder in S/S processes. Its widespread use in waste immobilization processes is attributed to its tolerance to wet material, non-flammability, durability in the natural environment as well as activator for pozzolanic additives. One most important aspect is its chemical fixation capability. The pH of plain hardened cement paste typically varies from 12.5 to 13.5, and is lowered slightly when pozzolan are incorporated. This high pH can be rationalized as follows. Water in excess of that needed for hydration is contained in the pores of the hardened cement paste. This “trapped” water in hardened cement paste contains dissolved sodium and potassium formally present in the cement. Since anions such as silicate, aluminate, and sulfate formed relatively insoluble cementing subtances during the hydraton reaction, the principal counter anion remaining is the hydroxide, OH ion. The high concentration of hydroxyl ion together with alkalis in the paste pore solution ensures that the cement pore fluids are alkaline. This condition also reduces the solubility of $Ca(OH)_2$. However, if alkalis are not present or eventually removed by leaching, the $Ca(OH)_2$ can solubilized. This large reserve of solid $Ca(OH)_2$ present in the cement acts as a buffer so that the internal pH of cement does not fall below 12.5. This high pH also favors immobilization as many metal hydroxides have a minimum solubility at high pH values (Macphee & Glasser, 1993).

The compounds present in cement results from the interaction during the burning of lime, silica, alumina and ferric oxide compounds which constitute the bulk of the raw mix, together with various minor compounds such as magnesia and alkalis. The clinker typically contains approximately 67% CaO, 22%SiO_2, 5% Al_2O_3, 3% Fe_2O_5 and 3% of other components. Less than 1% of CaO is present as free CaO. Portland cement is basically a calcium-silicate mixture, with four principal compounds i.e. tricalcium aluminate, or aluminate and teracalcium aluminoferrite or ferrite phase (Taylor, 1990). Other minor compounds present include MgO, TiO_2, Mn_2O_3, K_2O AND Na_2O. In addition to these, a small amount of gypsum [$CaSO_4$] is normally mixed with Portland cement to control the rate of setting caused by tricalcium aluminate. Table 2.4 shows the selected characteristics of the four compounds in Portland cement clinker.

Table 2.4: Principal compounds of Portland cement clinker and their characteristics

Approximate composition	$3CaO.SiO_2$	$2CaO.SiO_2$	$3CaO.AL_2O_3$	$4CaO.AL_2O_3Fe_2O_3$
Abbreviated Formula	C_3S	C_2S	C_3A	C_4AF
Common crystalline form	Monoclinic	Monoclinic	Cubic, orthohombic	Orthohombic
Percentage present	50-70	15-30	5-10	5-15
Rate reaction with water	Medium	Slow	Fast	Medium
Contribution to strength early age ultimate	Good Good	Low High	Good Medium	Good Medium

*Cement chemistry notion: C = CaO; S = SiO_2; H = H_2O; A = AL_2O_3; F = Fe_2O_3

(Jones, 1990)

2.6.1.2 Water and Soluble Constituents

Water is essential to initiate the hydration reactions. The water content, normally defined in terms of water to cement weight ratio (w/c), though cannot always be optimized in solidification, is critical to the final product. It is a major factor in determining the morphology of the hydrated cement paste. For flowable mixes, the w/c ratio normally lies in the range of 0.4 to 0.1, which is higher compared to water to the minimum w/c ratio of 0.25 for cement hydration (Glasser, 1997 and Lea, 1970). However, most investigators agree that complete hydration could not occur if the water to cement ratio is below 0.38 (Taylor, 1990). Nevertheless, water in excess of the minimum required for the hydration increase fluidity but also increases porosity and permeability of the cement-based waste forms. In waste solidification processes the w/c ratio must be kept as low in order to obtain a low permeability waste forms. In cases where the waste is in the form of liquid or semi solid, it may be desirable to maximize the waste to cement ration, thus high w/c ratio may be economical.

At very high w/c ratio, segregation of mix constituent may occur before set is achieved. Since Portland cement is categorized as hydraulic cement, it will continue to set under segregate water or ‘bleed water’. The appearance of bleed water may transient, since even well mixed slurries may segregate as set occurs. As such long term problem of matrix inhomogeneity may not be a problem. However, the presence of permanent bleed water in the solidification process is undesirable because is it not only mobile but contains the soluble waste contaminants.

The information of C-S-H gel in cement hydration is sensitive to the ionic strength and chemical constituent of the aqueous phase (Glasser, 1993). The presence of inorganic electrolytes and soluble organics in aqueous waste can alter the rate of set as well as the morphology of the hydrated products. Additionally the presence of species that form complexes with calcium, or which precipitate it by forming non-cementitious phases may delay set or prevents final set. Heavy metal salts has been reported to retard the setting of cement by precipitating hydroxides or other insoluble salts on the cement particles. Gypsum is purposely mixed with Portland cement to control the rate of setting by causing the precipitation of ettringite (Taylor, 1990, Lea 1970, and Portland Cement Association, 2001).

2.6.2 Pozzolanic Additives

ASTM C618 defines pozzolan or pozzolana as siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, react chemically with calcium hydroxide at room temperature to form compounds possessing cementitious properties. The properties of pozzolanic material are described in detail by Cook (1986) and Mehta (1981). The relatively higher degree of hydration of pozzolanic materials such as fly ash, silica fume and RHA I attributed to the high glass or amorphous phase content, high basicity and large specific surface area (for RHA and silica fume) (Cote, 1986, Swamy, 1986; Nontananandh, 1990). Studies have shown that the crystalline compounds hydrate at a much slower rate compared to the amorphous compounds but the reaction can be accelerated with grinding.

The use of pozzolan or mineral admixtures as constituent in cement or as cement replacement has drawn enormous attention. The main advantages of pozzolana cement over other forms of cement include resistance to seawater or sulfate solution, reduced heat hydration, better durability to sulfate and an acidic environment and their long-term high strength resulting from the reaction of silica with lime (Mehta, 1987; Douglas and Zerbino, 1986). The notable improvements achieved from the use of pozzolan include the service life of structure and economic advantages since most of these admixtures are waste products and thus easily obtainable and cheap. The use of industrial by-products such as RHA, fly ash, blast furnace slag or silica fume as admixtures is an important factor in waste stabilization/solidification. In comparing a well-hydrated Portland cement a paste and that of Portland-pozzolan cement, the later paste contains less calcium hydroxide and more C-S-H gel (Lea, 1970) Besides the increase in C-S-H gel, pozzolanic reaction enhance the chemical durability and mechanical strength due to pore refinement. Studies on pore size distribution by Mehta (1981) on 28-day, 90-day and one-year-old paste containing Santorin earth, a natural pozzolan, indicated a decrease in water permeability for cements containing 20/30% pozzolan at age 1 year when conversion of pores > 1000 Angstrom to smaller pores were almost complete. The addition of pozzolan in Portland cement results in a slower rate of setting and hardening, higher ultimate strength, lower heat of hydration and better performance in an acidic environment (Mehta, 1987).

2.6.2.1 Reactions of Pozzolanic Additives in Cement

The reactivity of pozzolanic additives depends on the reactivity of the glass phase (Bijen and Pletersen, 1994; Neville, 1995). The alkaline environment of cement enables its reaction with the glass phase found in pozzolanic materials. Pozzolanic processes involves siliceous and aluminosilicate materials. In a mixture of Portland cement, pozzolan and water, the amorphous or poorly crystalline oxides (SiO_2, Al_2O_3 and Fe_2O_3) present in the pozzolan will react with calcium hydroxide formed from the hydration of calcium silicates in Portland cement to form compounds with cementitious properties. The main pozzolanic-lime reaction involves the formation of calcium silicate hydrate (C-S-H) gel, similar to that in the hydration of Portland cement (Mehta, 1987). However, other cementitious products are also formed from the reaction between lime and alumina or ion oxide. The hydration products contain calcium aluminate hydrates or calcium aluminoferrite hydrates as well as calcium sulphoaluminate ferrite since gypsum is also present in the Portland cement-pozzolan mixture (Mehta, 1987).

Basically, a pozzolanic reaction involves the reaction of hydroxyl and calcium ions with SiO_2 or Al_2O_3-SiO_2 framework to form calcium silicate hydrate, calcium aluminate hydrate and calcium aluminate ferrite hydrates as shown in Equations 2.6, 2.7 and 2.8:

$$SiO_2 + Ca(OH)_2 + H_2O \longrightarrow CaO.SiO_2.H_2O \qquad (2.6)$$

Calcium silicate hydrate gel (Tobermorite gel)

$$Ca(OH)_2 + H_2O + Al_2O_3 \longrightarrow CaO.\ Al_2O_3.\ Ca(OH)_2.\ H_2O \qquad (2.7)$$

Calcium aluminate hydrate

$$Ca(OH)_2 + Fe_2O_3 + Al_2O_3 + H_2O \longrightarrow Ca(OH)_2.\ Al_2O_3.\ Fe_2O_3.\ H_2O \qquad (2.8)$$

Calcium aluminate ferrite hydrate

The degree of hydration of pozzolanic additive in the presence of lime depends on the chemical composition, morphology and amount of amorphous compounds it contain (Nontananandh, 1990). In contrast with the hydration of Portland cement, the pozzolanic reaction is slow, thus strength development in the presence of pozzolan is expected to contribute to long-term strength. Another primary difference is that pozzolanic reactions are lime consuming, while Portland cement hydration are lime-producing.

2.6.2.2 Types of Pozzolanic Additives

The commonly used inorganic additives used in S/S processes are rice husk ash, fly ash, silica fume and blast furnace slag. It is not the intention of this work to provide an exhaustive list of inorganic additives that have been used in S/S processes, but to provide some background on the materials commonly found in S/S processes.

Fly ash is commonly used as an additive in cement and in S/S processes. It is most often generated from the combustion of powdered coal in modern power plants. As coal passes through the high temperature zone in the furnace, the volatile matter and carbon are burned off. Mineral impurities such as clay, quartz and feldspar become fused and are transported to lower temperature zones where spherical particles are formed. Some of the mineral matter agglomerates to form bottom ash, but the majority of its flies out in the flue gas. This "fly ash" is subsequently removed by electrostatic precipitators, or bag filters. In a cement/fly ash system, the fly ash generally used as a bulking agent and a source of pozzolanic material. The particle size of fly ash range in size from 1 μm to 100 μm. the average particle size is 20 μm, which is similar to the average particle size of Portland cement. It uses decreases permeability, increase mix fluidity, lowers initial heat evolution, decrease pore pH and is an absorbent for metal ions. The C-S-H formed in cement/fly ash system is more amorphous, contains more aluminum and has as Ca:Si ratio lower than that of Portland cement system.

Silica fume or condensed silica fume is used in cement/silica fume systems to increase the silica content while maintaining the concentration of other reactive oxides unchanged. It is a byproduct of the production of metallic silicon or ferrosilicon alloys. At high temperatures (~20000C), quartz is reduced to silicon, forming gaseous SiO_2. The gas is transported to lower temperature zones and condenses when in contact with air to form spheres of noncrystalline silica. The material formed is extremely fine and is removed by filtering the outgoing gases through bag filters. Silica fumes in a cement/silica fume system are normally used to decrease permeability, and increase sorption of both metals and non-metals, particularly alkalis. The C-S-H gel formed has low Ca:Si ratio (Cheng-yi, 1985).

Another commonly used additive is blast furnace slag or BFS. It is a byproduct of the production of metals such as iron, steel, copper, lead, etc. The liquid slag is formed by quickly quenching the slag material from the process at temperatures of 1400-1500ºC in water or combination of water and air. This will keep most of the lime, magnesia, silica, iron, and alumina oxides in an amorphous or glassy phase. BFS is often referred to as granulated BFS when it is quenched by water and as pelletized slag due to the pellets formed. Blast furnace slag in cement/BFS system reduces permeability, lowers the internal solution redox potential i.e. from oxidative to reductive conditions are beneficial because these aid in the retention of mobile species at higher redox conditions through species reduction. The C-S-H produced in cement/BFS system has low Ca:Si ratio and sulfoaluminates than cement system.

2.7 Immobilization/Containment Mechanism

The main aim of stabilization/solidification process is to immobilize the contaminants in the waste so as to resist leaching to the environment. The mechanism by which waste constituents (inorganic and organic) interact with cement matrices is important in predicting the long-term effects of solidified waste forms. The mechanism of fixation for the three primary groups of pollutants (metals, other inorganics, and organics) differ from one another (Conner, 1990). The major containment mechanisms that immobilize the contaminants in the waste form were reviewed by Malone and Larson (1983) and Conner (1990). These include pH control, redox potential control, hydroxide precipitation, carbonate precipitation, sulfide precipitation, silicate precipitation, complexation, adsorption, chemisorption, passivation, diadochy, reprecipitation, ion exchange, encapsulation and alteration of the waste property. In a solidified system, the waste contaminants may chemisorb, precipitate, form a surface compound to any of the several cement component surfaces, form inclusions or be chemically incorporated into the cement matrix or simultaneously occurrence of the several possibilities (Cocke and Mollah, 1992).

The reaction between waste constituents and cement is very complex. Macphee and Glasser (1993) presented a periodic table in which elements were divided based on their solubility properties in cementitious systems and to show the interactions between cement and the elements at pH of ~ 12 – 13. The group I elements, the alkalis, remain soluble. The bulk of the elements, however undergo reaction in the alkaline environment of cement. These reactions can be distinguished between rapid reaction occurring during setting and hardening and those which occur slowly, over a longer period of time (Glasser, 1994). These elements can exhibit a range of reactions, depending on the concentration and time of study. At low concentration, below threshold of precipitation, sorption is likely to dominate the species present between aqueous pore fluid and solids. C-S-H, with its high surface area preferentially sorbs anions at high Ca:Si ratio but at low Ca:Si ratio, cationic sorption might be favoured.

The inorganic species encountered in waste S/S can be classified as species soluble in alkaline conditions, insoluble and amphoteric (Glasser, 1997). The first type of species will not precipitate whereas the intermediate and amphoteric, are relatively insoluble at near-neutral pH. However, its solubility increases in both strongly acidic and strongly basic pH. The precipitation often involves two or more steps. At a high pH a hydrous oxide or hydroxide may precipitate, but the waste constituent may react with cement components such as Ca, Al, Si or OH- to form a more complete precipitation. This secondary reaction takes a longer time and results in the formation of solubility- limiting phases (Glasser, 1994). The amphoteric behavior of many elements, is suppressed by the formation of compounds. As a result they remain relatively insoluble in the cement-conditioned environment. Only a few of the elements shown in the periodic table have been studied with respect to their behavior in a cement environment. Further research is needed to better understand the behavior of elements and the mechanism of interaction in a cement environment.

2.8 Interference Mechanism

S/S processes can be affected by the chemical constituent present in the waste being treated and by many other factors such binder-to-waste ratio, water content or ambient temperature. The interferences caused by the chemical constituents of the waste can affect the S/S of the treated product. General type of interference caused by the chemical constituents include inhibition of bonding of the waste material to the S/S material, retardation of setting, reduction of stability of the matrix resulting in increased potential for leachability of the waste, and reduction of physical strength of the final product (US EPA, 1990).

2.8.1 Interferences with Solidification

The contaminated materials usually treated by S/S processes are widely fluctuating, complex mixture. Even with one waste source, the concentrations can vary by a factor of ten or more from batch to batch. Many waste constituent affect cementation chemistry by altering setting rate of the properties of S/S treated waste. Depending on the contaminant type and concentration, setting rate may be increased or decreased. As an example of concentration effects, mild accelerators such as chloride or nitrate anions can slow setting at higher concentrations. Treated waste properties such as porosity or flexural and compressive strength may be reduced by contaminant (US EPA 1990).

2.8.2 Interferences with Stabilization

Interferences with stabilization include chemical incompatibilities and undesirable reactions. Generally, the types of effect such as decreasing the UCS, retard setting and curing, increase setting, decrease durability of cement, and weaken bonds between waste particle and cement releases of noxious gases or effects resulting in the increased leaching potential of the contaminants (US EPA, 1990).

The ability of a stabilized/ solidified waste product to retain a given hazardous constituent depends primarily on its long-term durability or strength and on its resistance to leaching of waste constituents.

2.9 Durability of Stabilized/Solidified Waste Forms

Various chemical and physical tests are performed on the treated wastes to determine whether the waste forms are acceptable for transportation and landfilling operations as well as its leachability characteristics. These tests are somewhat technology oriented and are mostly designed toward evaluating the solidified waste forms disposed of in sanitary landfills. As such, the types and extent of testing are normally left to the discretion of the company involved in the solidification process.

2.9.1 Physical and Engineering Properties

The main objective of S/S treatment is to reduce the mobility of contaminants as well as to minimize free liquids. These objectives are accomplished in cement-based processes through the formation of a monolithic solid that incorporates the waste materials and immobilized contaminants. The environmental stability of the S/S is dependent on the chemical and physical properties of the cementing materials used in the process. The physical properties of the waste are modified by the stabilization/solidification processes. The end product of many treatment processes can be a granular soil-like material or a monolithic solid block resembling low-strength concrete. Testing methods adapted from the soil and concrete fields have been used to assess their physical properties so that its durability under field condition can be predicted.

The physical properties of stabilized/solidified waste are commonly employed as indicators of the degree of containment of chemicals, and to an extent, are used to predict durability in field conditions and long-term physical characteristics. Physical tests are aimed primarily at a) determining particle size distribution, porosity, permeability and wet and dry densities, b) evaluating bulk properties, c) predicting the reactions of materials to applied stress in landfills, embankments, etc. and d) evaluating durability. Five standardized physical tests are frequently applied to stabilized/solidified products. (US EPA, 1982a). These are bulk and dry unit weight, unconfined compressive strength, permeability, wet/dry durability, and freeze/thaw durability.

2.9.1.1 Bulk and Dry Unit Weight

Bulk and dry unit weight is a measure of density and indirectly, of void volume. The bulk unit weight is obtained by measuring the weight is obtained by measuring the weight (solids plus liquid) per unit of total volume of material mass. The dry unit weight is obtained from the ratio of the oven-dried weight to the total volume. Cote (1986) reported the bulk density to vary between 1.25 and 1.75 g/cm^3 while the water content for the same samples, based on wet weight basis varied from 0.14 to 0.50 (w/w).

2.9.1.2 Unconfined Compressive Strength (UCS)

S/S materials must have adequate strength to enable them to support the load of other materials placed over them. Further, the test result would be expected to correlate with the effectiveness of stabilization of inorganic waste as the inorganic are encapsulated in the hydrating matrix.

In general, for any given stabilization reagent, the stronger the stabilized hazardous waste, the more effective the stabilization process, particularly for inorganic contaminants. Thus, the UCS is often used as an indicator parameter of the effectiveness of stabilization (La Grega, 2010).

Unconfined compressive strength measures the compressive strength and the shear strength of a monolithic matrix. The shear is obtained by multiplying the unconfined compressive strength by 0.5. It is an important property especially when the solidified waste forms are recycled/reused as construction materials. It gives an indication on the ultimate bearing capacity of the treated wastes.

The US EPA considers 0.34 MPa (50psi) as a satisfactory Unconfined Compressive Strength for stabilized/solidified material (US EPA, 1982b). This suggested minimum guideline is to provide a stable foundation for materials that are placed upon it, including construction equipment and impermeable caps and cover material. However, the minimum required strength should be determined from the design loads to which the material may be subjected (LaGrega, 2010). The strength requirement for solidified products in the UK, as required by the Waste Regulation Authority, is 0.7 MPa for 28-day strength (Hills and Pollard, 1997). The strength of various sludges solidified using cement-based process at the Wastewater Technology Center ranged between 0.068 MPa to 0.52 MPa (Cote, 1986). Hills *et al.* (1993), in study using acid and alkaline inorganic filter cake waste reported a 28-day strength of 13.5 MPa and 0.1 MPa for 5% and 30% waste content respectively using a cement-fly ash matrix. Table 2.5 lists the waste performance characteristics required by the Waste Disposal Authority, United Kingdom (Sollars and Perry, 1989).

Table 2.5: Specimen Solidified Waste Performance Characteristics Required by the Waste Disposal Authority, U.K.

Characteristic	**Requirement**	**Comparative values**
Compressive strength (28-day)	≮ 0.34 MPa	Concrete: 30MPa Mortar:20 MPa Grouts: 0.5-4 MPa
Leachate Quality*	pH 8 – 11 Toxic heavy metals: Zn < 10 g/m^3, Hg < 0.5 g/m^3 Others (Cd, Cr, Cu, Ni, Pb, Ba, Co, V, Mb, Sn, As, Se, Sb): 5 g/m^3 total	-NA-

Note: NA – not applicable

*-50 g solidified waste (age 28 days) are ground to a fine powder, stirred for 1 hour with 500 ml distilled water and filter through Whatman No.2 filter paper.

(Adapted from Sollars and Perry, 1989)

2.10 Leachability of Solidified Waste Forms

Leachability is the main factor in appraising the degree of immobilization in the stabilization/solidification of hazardous waste. It is important in evaluating the safety of the S/S product's acceptability and environment impacts of the contaminants from the solidified waste forms. As such leaching tests are essential in the environmental assessment of stabilized wastes.

In the United States the environmental acceptability of hazardous waste for land disposal is based on the Toxicity Characteristics Leaching Procedure (TCLP) test. It is extensively used as a basis for evaluating the effectiveness of the S/S process and serves as a regulator criterion for delisting purpose. It is a stringent testing procedure using acetic acid buffers as the leachant, simulating aggressive conditions to which the solidified waste forms will encounter in a commingled municipal land fill.

However, the evaluation based on TCLP test do not take into consideration the long term degradation of the materials due to environmental corrosion and permeable nature of the cement solidified waste forms. Kualiti Alam Sdn. Bhd., which manages the treatment and disposal of hazardous waste in Malaysia also adopts the TCLP regulator limits as well as limits stated in Standard B of the Malaysian Water Quality Standards for landfill disposal of the hazardous waste. Table 2.6 shows the guidelines for disposal of scheduled waste at the Bukit Nanas scheduled waste treatment and disposal center.

Table 2.6: Guidelines for disposal of scheduled waste directly to Kualiti Alam landfill

Parameter	Method	Limits (mg/l)	Comment
Smell/odour			Waste to be disposed not have smell which can cause serious air pollution at landfill

(Kualiti Alam, 2001)

Table 2.6 continued

Parameter	Method	Limits (mg/l)	Comment
pH when mixed with distilled water after TCLP extraction	APHA	5.5 -12	Too acidic/alkaline condition will release heavy metals.
As	APHA	5 mg/l	US EPA Limit
Ba	APHA	100 mg/l	US EPA Limit
B	APHA	400 mg/l	US EPA Limit
Cd	APHA	1 mg/l	DOE Standard B limit based on 100x dilution
Cr	APHA	5 mg/l	US EPA Limit
Cu	APHA	100 mg/l	US EPA Limit
Pb	APHA	5 mg/l	DOE Standard B limit based on 100x dilution
Hg	APHA	0.2 mg/l	US EPA Limit
Ni	APHA	100 mg/l	US EPA Limit
Se	APHA	1 mg/l	DOE Standard B limit based on 100x dilution
Ag	APHA	5 mg/l	US EPA Limit
Sn	APHA	100 mg/l	DOE Standard B limit based on 100x dilution
Cl^-	APHA	2 %	Drinking water quality based on 100x dilution
Total organic carbon	APHA	< 10%	
CN-	APHA	0.5 mg/kg	Waste at landfill should not contain cyanide
Oil and grease	APHA	1000mg/kg	DOE Standard B limit based on 100x dilution
Pressure of Fumes/gas			Waste must not release fume or vapour at any significant level.
Pressure of Liquid/water			Free liquid/water is not accepted.

(Kualiti Alam, 2001)

US EPA provides a list of regulatory leaching levels for metals for toxicity, characteristics, delisting, drinking water, multiple leachates and lowest best demonstrated available technology (BDAT) as shown in Table 2.7.

Table 2.7: US EPA Regulatory Leaching Levels

Maximum concentration in TCLP extract (mg/l)					
Metal	Toxic characteristics	Delisting	Drinking water	Leachate Multiple source	Lowest BDAT
Arsenic	0.5	0.315	0.05	5.0	5.0
Barium	100.0	6.3	1.0	52.0	52.0
Cadmium	1.0	0.063	0.01	0.066	0.066
Chromium	5.0	0.315	0.05	5.2	0.073
Lead	5.0	0.315	0.05	0.51	0.021
Mercury	0.2	0.013	0.002	0.025	0.025
Nickel	NA	2.205	NA	0.32	0.088
Selenium	1.0	0.063	0.01	5.7	5.7
Silver	5.0	0.315	0.05	0.072	0.072

TCLP is also the test required by Malaysian Department of Environment (DOE) implementing regulation for determining toxicity of waste (Table 2.8).

Table 2.8: Maximum Concentration of Selected Contaminants for the Toxicity Characteristic Leaching Procedure

Contaminants	**Maximum Level (mg/L)**
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Silver	5.0

(DOE, 2005)

2.10.1 Leaching Test

Leaching is the process by which contaminants are transferred from a stabilized matrix to a liquid medium such as water (La Grega *et al.,* 2010).

The potential impact on the environment of solidified waste form disposed on land normally assessed and predicted using bench scale laboratory leach test. The objective of leaching tests is to provide assessment of pollutant release from a solid material (i.e. solidified waste form) to the surrounding environment. Leachability is assessed by carrying out a leach test to directly measure the release of pollutants into an aqueous medium as a function of time. Two disposal scenarios for the solidified waste can be considered. In a well-managed disposal scenario, the solidified wastes are well buried below the depth of frost penetration (Cote and Hamilton, 1983). In this manner, the wastes is expected to maintain its physical integrity.

The leaching medium is ground water or infiltrated rainwater that is well buffered by the interaction with the topsoil. The rate of flow of the leaching medium is low. Water contact with the waste forms may occur in two ways i.e. percolation through the wastes and water flow around the waste or through fractures (Moszkowicz *et al.*, 1998). In a mismanaged disposal scenario, the solidified wastes are subjected to weathering. Studies have shown that solidified wastes can break down after a few cycles of freezing and thawing.

Leach tests are often used to simulate leaching conditions under well-managed landfill conditions (Cote and Hamilton, 1983). Different types of leaching test have been carried out which can be grouped as extraction tests, static leach tests and column leach tests (US EPA, 1989).

In an extraction test the ground or pulverized waste forms is agitated in a neutral or acidic leaching medium. Extraction tests such as the US EPA TCLP test are generally used to stimulate “Worst-case” leaching conditions to which the solidified waste forms would encounter in a commingled municipal landfill (US EPA, 1989). Leach tests on monoliths specimen on the other hand do not involve any agitation and can be performed under static, semi-dynamic or flow through leaching conditions.

Static leach tests do not require leachant replacement and are used to determine the solubility limits of the contaminants. Both the semi dynamic and flow through tests provide a measure of the net forward leach rate, expressed as a diffusion coefficient (Fuhrmann and Colombo 1990).

Column leach test involve placing the pulverized waste in a column and allowing the leaching medium to continuously flow through the column. Even though this is considered to be more representative of field leaching conditions but is not widely used dues to poor data reproducibility (US EPA, 1989).

The leaching mediums commonly used are deionized water, organic acids, inorganic acids and seawater. Ideally, the leaching medium used should simulate that which is actually in contact with waste in the landfill (Conner, 1990b). Weak organic acids are used in many leach tests to accelerate the leaching rates as well as simulate acid rain (Cheng, 1991). Additionally, the use of mildly acidic solutions of carbonic acid or acetic acid has some basis in natural systems. CO_2 in soil water affects the acidity of the soil. Carbonic acids is formed naturally when CO_2 dissolved in water according to equations 2.9 and 2.10 below:

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \tag{2.9}$$

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \tag{2.10}$$

Pure water in equilibrium with atmospheric CO_2 (0.03%) has a pH around 5.6, which is mildly acidic. However, the activity of microorganisms and subsequent aerobic biodegradation of organic material in soil could result in the production of CO_2. In the topsoil, the soil air concentrations of CO_2 exceed 1 % resulting in a pH of approximately 4.9 (Boardman, 1999).

In the presence of carbonic acid, calcium in the pore solution will leach out. Calcium hydroxide in the cement paste dissolves and leads to the precipitation of calcium carbonate. As more calcium carbonate, as more calcium hydroxide is consumed, more Ca_2^+ ions will be available through decalcification of C-H-S gel for the precipitation of $CaCO_3$.

Long term CO_2 attack will eventually soften the C-H-S gel and decomposed it to $CaCO_3$, acidic-insoluble silica gel and water (Bonen and Sarkar, 1995):

$$\text{C-S-H} + HCO_3^- \longleftrightarrow CaCO_3 + SiO_2(\text{gel}) + H_2O \qquad (2.11)$$

The most common leaching tests are listed in Table 2.9. To ensure maximum extraction of metal from the leaching process, solution concentration and purification shall be carried out using precipitation, cementation, solvent extraction and ion exchange (La Grega et al, 2010).

The physical strength of cement-based S/S treated waste develops in period of several days. In that duration, many of the chemical reactions that cause immobilization rapidly occur. Therefore, 28 days of sample curing is not as critical for leaching tests, but sample size reduction is particularly required. The major issues in selecting a size reduction approach in the leaching test are to avoid contaminant of the sample, to avoid partitioning of contaminants into a specific size fraction, and to avoid contaminant loss, particularly volatile organics.

Table 2.9: Types of Leaching Test

- Paint Filter Test
- Liquid Release Test
- Extraction Procedure Toxicity Test
- Synthetic Precipitation Leaching Procedure (SPLP)
- Equilibrium Leach Test
- Dynamic Leach Test
- Multiple Extraction Procedure
- Toxicity Characteristic Leaching Procedure (TCLP)
- Modified uniform leach procedure (ANS 16.1)
- Sequential Leach Test-Sequential Chemical Extraction

(Adapted from La Grega, 2010)

The typical steps for size reduction are sample fragmentation, grinding, and sizing. Fragmentation is best done with hammer and anvil and should be small in quantities to avoid metal contamination of the waste. Grinding can be done with agate, dense alumina or tungsten-carbide equipment. Mortar and paste or mechanical grinder can be selected based on sample throughout in the laboratory.

The choice of technique for leach testing depends on the company or agency handling or testing the waste. Even there are numbers of leaching tests available, however, there is no standardized leach test that can adequately predict the impact of a stabilized/solidified waste on the environment. Table 2.10 gives a summary of types of leaching tests from various countries.

Table 2.10: Summary of Leach Tests from Selected Countries

Leach test	Particle size (mm)	Leachant	Length of extraction	Shaking technique	Solid leachant ratio
US EPA Toxicity	9.5	Deionized water (buffered with 0.5M HAc to pH 5 0.2)	24 hr (± 4 hr)[a]	End-over-end using rotary extractor	100g/1600ml
TCLP	9.5	#1: HAc/NaAc (pH 4.93 + 0.05) #2: HAc (pH 2.88 ± 0.05)	18 ± 2 h	End-over-end	1:20[b]
UK[c]	<2.00 <2.00	Deionized water 0.5 M HAc	1 hr 1 hr	Shaker	1:10 1:10
Japan	5.00	Deionized water pH between 5.8 and 6.3 pH between 7.8 and 8.3 (for reclamation alongside of seashore)	6 hr	Shaker	1:10
France NFX31-210 (Mehu et al., 1991)	4	Demineralized water	16 hr	Stirring (60/min)	1:10

a – A further 4hr extraction is required if pH of final mixture after 24 hr extraction is >5.2

b – The differences between TCLP and EP Toxicity are the inclusion of additional 38 chemicals, the use of extraction fluid #1 and #2 and the use of Zero-headspace Extractor for volatile analytes.

c – For samples containing 100 % solids only. The weight of extraction fluid can be calculated as follows:

$$\text{Weight of extraction fluid} = \frac{20\ x\ \%\ solids\ x\ weight\ of\ waste\ filtered}{100}$$

2.10.2 Leaching Mechanism

The leaching mechanism that can control leaching rates under various conditions or at different times during a leaching process have been reviewed by Conner *et al.* (1990a). Factors that could affect the leaching potential of the solidified waste can be categorized as external factors and intrinsic factors (Conner, 1990b) External factors are those governed by the designated disposal (Landfill) environment and include factors such as the amount of precipitation, ground water flow and geological conditions, temperature and the chemical potential and acidity of the rain and ground water. Intrinsic factors on the other hand are those inherent to the solidified waste forms and include chemical speciation of the pollutants in the matrix, solubility, alkalinity, redox potential, mechanical strength, permeability, porosity, tortuosity and durability (Josephson, 1982).

A cement- based waste form consist of several solid phases, a liquid phase (pore water) and air voids. Prior to being exposed to an aqueous leaching solution, the chemical species in the solid phases and in the pore solution are in a state of chemical equilibrium (Cote, 1986). Upon contact with the leaching medium, the difference in chemical potential between the solid and the leaching solution causes a mass flux between the solid surface and leachant. This in turn creates concentration gradients that include bulk diffusion through waste from matrix (Conner, 1990b; Cote, 1986). Species from the leachant also interact to form new species both in the aqueous solution and in the solid.

Leaching can be as the process in which a waste component is removed chemically or mechanically into solution from the solidified waste matrix by the passage of solvent such as water (Poon, et al., 1985a). A solidified waste form is a porous solid that is partially saturated with water, with one or more solid phases, entrapped air (air voids) and a liquid phase (pore solution). All three phases are in chemical equilibrium or close to equilibrium. This equilibrium is disturbed when the waste form is exposed to leaching conditions. The resulting difference in the chemical potential between the leaching medium and the surface of the solid will result in concentration gradients that include bulk diffusion in the solid (Conner, 1990). Besides bulk diffusion, chemical reactions between the solids constituent and the leaching medium can also take place.

For a waste constituent to leach, it must first dissolve in the pore water or in the leachant permeating the solid matrix. Cheng (1991) idealized leaching mechanism of metals as occurring in five steps.

(i) Mass transfer of acids from bulk liquid to solid surface

(ii) Transport of acids through leached layer

(iii) Diffusion-controlled fast dissolution reactions at leaching boundary

(iv) Transport of metals through leached layer

(v) Mass transfer of metals from solid surface into bulk liquid

2.11 Bricks

Brick is one of the oldest construction materials, which was used for all kind of building applications e.g. structural elements and infrastructures, especially for sufficient compressive strength in combination with good acoustic and thermal properties with low construction costs and fast in erection. Examples of commonly used materials for bricks are sand-cement bricks, clay bricks and calcium-silicate bricks.

2.11.1 Size of Bricks

The brick are normally shaped as rectangular prisms but special shapes, some of which are in such general use as to be known as “standard specials”, are produced as required. Brick can be solid, perforated, hollow or cellular and are acceptable for different construction purposes within a range of compressive strength and resistance to water and corrosive fluids. The dimension of brick can be defined as a masonry unit with dimensions (mm) not exceeding 337.5×225×112.5 (l×w×t). However, BS EN 771-3 specified that the standard size of a brick shall be 215 × 102.5 × 65 mm.

2.11.2 Classification of Bricks

BS EN 771-3 classifies bricks in three categories which are Common Bricks, Facing Bricks and Engineering Bricks.

a) Common Bricks

Common brick are the normal brick which are used as structural materials and typically are strong and durable. Normally this type of brick is plastered and it is non-bearing loading. It also is the cheapest brick available in construction market.

b) Facing Bricks

Facing brick is used for facing purpose and available in different colour, sizes and textures. It is free from imperfection such as crack and very durable.

c) Engineering Bricks

It is used for load-bearing purposes such as pier or on the wall or in a brick that requires specific resistance. Examples such as "Staffordshire Blues", it is made from clay that consists of 8 to 10% iron oxide and baked at very high temperatures and produce glass and hard surface and high density. The engineering brick have good resistance to frost and to water, making them ideal for groundwork's, sewer works and retaining walls. A common type of engineering brick is the Accrington brick; it is an iron hard engineering brick that was famously used for the foundations of the Empire State Building.

2.11.3 Engineering Properties of Bricks

BS EN 771-1:2011+A1:2015 listed the engineering properties of bricks as compressive strength, density, water absorption and durability.

a) Compressive Strength

The compressive strength is a mechanical property used in brick specifications. Commonly, compressive strength decrease with increasing porosity but strength is also influenced by clay composition and firing (Applied, 2008). Engineering brick has specific requirement relating to absorption and strength in extra to those such as dimensional tolerances and efflorescence requirements which apply to other types. The compressive strength of traditional engineering brick, which are categorized in grade A and B is not less than 70 N/mm^2 and 50 N/mm^2 respectively compared to clay brick which is only 5 N/mm^2 (Hendry, 2004).

b) Density

The density of the brick will affect other properties such as compressive strength, durability, thermal conductivity, and porosity. It may vary due to the mineral composition and workmanship during the production of the brick. Average density of clay bricks ranged between 1826 and 1985 kg/m^3, sand-cement bricks about 2085 kg/m^3 and engineering bricks 2200 to 2350 kg/m^3.

c) Water Absorption

The water absorption of brick is depending upon their porosity. A good quality brick does not absorb water greater than one-seventh of its self-weight (BS3921:1985).

d) Durability

The durability of a material is the ability to withstand a particular recurrent weathering effect without failure. Durable brick will retain its original form, quality, and serviceability when exposed to environment. Factors responsible for deterioration of bricks are freezing and thawing, aggressive chemical exposure, abrasion, high temperature and poor workmanship.

2.11.4 Usage of Copper Slag in Bricks

As no research has been done on the usage of abrasive blasting waste in bricks, reviews were done on similar waste, copper slag. Table 2.11 summarize recent researches on the utilization of copper slag in bricks.

Table 2.11: Previous Research Findings on Copper Slag in Bricks

Author	**Nature of Study**
Mahendran *et. al* (2017)	This research reviewed the potential of recycling various waste like copper and rice husk ash (RHA) in bricks production as partial replacement of red soil in raw material mixtures. The experiments are conducted for variation in properties i.e, compressive strength, water absorption, hardness and soundness. Compressive strength (range 3.6-4.8 N/mm^2) and the water absorption of bricks (range 5%-20%) were reduced when the red soil is replaced by RHA and copper slag as the percentage of substitution increases. Average density are within the range of 3.4-3.6 kg/m^3.

Table 2.11 continued

Author	**Nature of Study**
Velumani *et. al* (2016)	In this research, fine aggregate is replaced by copper slag and coarse aggregate is replaced by discarded tyres in order to produce concrete bricks with size of 19 cm x 9 cm x 9 cm. 0% to 100% of copper slag (by weight) replacement for fine aggregate, 0% to 50% of fly ash (by weight) as replacement for the cement and the coarse aggregate is fully replaced by discarded tyres. The research work is still on-going.
Kanagalakshmi *et. al* (2015)	A study was made to evaluate the technical possibilities of incorporating fly ash, copper slag, marble dust and gypsum in the construction bricks. Unit weight, compressive strength, water absorption and efflorescence values has been compared with conventional building material. The compressive strength is within the range of 6.9-7.3 N/mm^2 while the water absorption within the range of 8.2-10.7%.

2.12 Concrete

Concrete is mixture of materials consisting of cement, water and aggregates. Depending on the properties needed from the concrete, other materials can be added, such as reinforcements to increase the tensile strength of the concrete and the use of superplasticiser to increase workability. Once all the constituents of the concrete has been mixed together using a concrete mixer machine or manually, the fluid mass is placed into its formwork and is allowed to cure in order to gain strength. The concrete is usually considered of having density of 2400 kg/m^3 of conventional crushed stone aggregate (Teo et al. 2006). The compressive strength is the most commonly used parameter to describe the quality of concrete in practice (Wiegrink et al., 1996).

2.12.1 High Strength Concrete

Prior to the early 1990's, it was commonly agreed that a concrete with at least 41.7MPa of compressive strength is the measure for high strength concrete (Myers, 1999). However, in the FIP/CIB (1990), HSC is defined as concrete having a 28-day cylinder compressive strength of 60MPa (Rashid and Mansur, 2009).

2.12.2 Curing of Concrete

It is well-known that among the factors influencing the strength development of concrete is the curing environment where curing is usually done in a fully saturated condition to ensure proper hydration of the cement over time, therefore leading to a significant strength development. The rate of hydration is negatively affected by high temperature and lower ones lengthen the hydration process leading to poor strength development (Mannam et al. 2002).

2.12.3 Usage of Copper Slag in Concrete

As no research has been done on the usage of abrasive blasting waste in concrete, reviews were done on similar waste, copper slag.

Previous research papers of Bipra *et al* (2003) and Shi *et al* (2008) reviewed the potential use of copper slag as a partial substitute of cement and aggregates in concrete. The effect of copper slag on the hydration of cement based materials was investigated by Mobasher *et al* (1996) and Tixier *et al* (1996). The pozzolanic activity of copper slag has been investigated by Pavez et al (2002). Akihiko *et al* (1996) suggested that copper slag can be used as a replacement for fine aggregates in order to obtain a concrete with good strength and durability requirements and also in further research by Ayano *et al* (2000) has clarified the strength, setting time and durability of concrete with copper slag will be improved when fine aggregate is replaced with copper slag.

2.13 Summary and Research Gap

Malaysia is categorized in the 20 most important maritime nations of the world. Hence, activities are increasing in the shipbuilding and repair work industry. Abrasive blasting waste originating from shipbuilding and repair works is classified by DOE as ‘schedule waste’ code SW 104, which also known as hazardous waste in other countries. In 2015, DOE reported that SW 104 was the highest category of scheduled waste generated in the country. Stabilization/ solidification (S/S) technology is chosen to treat the hazardous waste such as ABW because besides lowering the leaching rate, the technique reduces the sludge’s toxicity and facilitates handling prior to disposal area. Cement is the most adaptable binder for the immobilization of hazardous waste in S/S technique. The end product of many S/S treatment processes can be a granular soil-like material or a monolithic solid block resembling low-strength concrete. However, interference mechanism may affect the S/S processes in terms of inhibition of bonding of the waste material to the S/S material, retardation of setting, reduction of stability of the matrix resulting in increased potential for leachability of the waste, and reduction of physical strength of the final product. The success of S/S treatment depends on the compressive strength and leachability as they are the main factors in evaluating the degree of immobilization in the stabilization/ solidification of hazardous waste.

The potential stabilized and solidified ABW may be explored as a new construction material such as brick and concrete. However, none of the previous researches investigate the potential of copper slag after it has been used as an abrasive blasting media and none of the researches explored the possibility of using ABW in bricks or concrete due to its hazardous characteristics. Hence, literature reviews were done on the usage of similar waste, copper slag as replacement for cement and aggregates in bricks and concrete.

CHAPTER 3: MATERIALS AND RESEARCH METHODOLOGY

3.1 Materials

The constituents used in the S/S formulation are Ordinary Portland cement, ABW and tap water. Sand was added in the design mix to produce cement-ABW bricks while gravel was used as coarse aggregate in the ABW concrete.

Other chemicals such as glacial acetic acid and nitric acid were used as part of the testing regime.

3.1.1 Abrasive Blasting Waste (ABW)

Abrasive blasting waste samples were collected from an operational ship repair yard located at Pasir Gudang, Johor Darul Takzim once in 12 months due to long haulage. Sample taking was done for a number of batches to verify on the homogeneity of the waste. The waste was kept in heavy-duty plastic bags and placed in covered metal containers in the laboratory at the room temperature during the period of study. Microstructure analysis of the abrasive blasting waste was carried out using scanning electron microscope (SEM) and energy dispersive x-ray (EDAX). BET test has also been conducted to identify the level of porosity of the waste. The physical properties e.g. particle size, colour, specific gravity and water absorption and chemical properties of the abrasive blasting waste are discussed in Chapter 4.

3.1.2 Cement

Locally produced ordinary Portland cement (OPC) that conformed to MS: 522: Part 1: 2003 (YTL) was used throughout the experimental investigation. The OPC was produced by YTL Cement Bhd. The cement used was kept in an airtight container to prevent absorption of moisture and to avoid chemical reaction. Preliminary tests of the cement was explained in Clause 3.2.7 and Clause 3.2.8 and conducted to achieve the required workability of fresh concrete. The chemical composition of the cement used is shown in Table 3.1.

Table 3.1: Chemical composition and physical properties of OPC

Tests	Units	Specification MS 522-1:2007(32.5N)	Test Results
		Chemical Composition	
Sulfate content (SO_3)	%	3.5 max	2.04
Chloride (Cl)	%	0.01 max	0.01
		Physical Properties	
Setting time (Initial)	mins	Not less than 75	185
Soundness	mm	Not more 10	<1
Compressive Strength (Mortar Prism)(1:3:05) : 7 days	MPa	Not less than 16	18
Compressive Strength (Mortar Prism)(1:3:05) :28 days	MPa	32.5 < x < 52.5	36

(Provided by the manufacturer, YTL)

3.1.3 Mixing Water

Besides causing the chemical reaction of cement, water lubricates the mix for better workability. Deionize water was used for preparation of standards, acid solutions and leachability tests as well as for mixing the ABW and cement. Ordinary clean tap water was used in the process of making the brick and concrete. Distilled water was used for rinsing of glassware and tool.

3.1.4 Fine Aggregates

Only fine aggregates were used in producing cement-ABW bricks. The sand was sieved to ensure the fine particle in it was free from unwanted particles. The sand was air-dried to remove moisture in atmospheric temperature. Grading was determined by passing aggregates through a set of standard sieves. Local mining sand with particle density of 2.4 to 2.7 was used as fine aggregates during the production of bricks and concrete. The sand obtained was sieved passing the aperture of 4.75 mm. The sieve analysis of fine aggregates was conducted according to the BS EN 933-1:2012. The specific gravity and absorption tests were done as specified in ASTM C128 – 15:2004.

3.1.5 Coarse Aggregates

Crushed granite with angular shape and rough surface texture was used as coarse aggregate in the production of the concrete. The size of granite used was in the range of 5mm to 20mm. It was washed to eliminate the dust and dirt on its surface and air dried before using. The specific gravity and absorption tests were done as specified in ASTM-C127:2004.

3.1.6 Chemicals

The chemicals used include glacial acetic acid and nitric acid. 100% purity acetic acid from Merck was used for the preparation of leachant for the leachability tests while 65% purity nitric acid was used for digestion of waste and preparation of standard solutions for metal analysis, preservation of leachates as well as for washing glasswares, sample bottles and Perspex moulds.

3.1.7 Mould

50 mm x 50 mm x 50 mm (ASTM, 2005) perspex mould was used for casting unconfined compressive strength (UCS) paste block while 215 mm × 102.5 mm × 65 mm Perspex mould was used to cast bricks. Mould for concrete block was made of steel with

dimension of 150 mm x 150 mm x 150 mm. Whole block leaching sample is cast in Perspex mould of 24.3 x 24.3 x 24.3 mm (ANSI, 2003). All moulds were cleaned from any contaminant by washing and rinsing with 5% nitric acid solution and distilled water before used.

3.2 Characterization and Evaluation Test of Materials

The tests elaborated in this section are used to characterize the materials before and after stabilization and solidification (S/S) treatment. The test methods and its objective are summarized as follows.

3.2.1 Microstructural Examination by SEM-EDAX

The morphology of the S/S specimen was examined using a Philips XL40 Scanning Electron Microscopy (SEM) for better understanding on the nature of the stabilization processes at work. The microstructural analyses are part of basic research into stabilization mechanism.

Philips XL40 is also equipped with Energy Dispersive X-ray analysis (EDAX) which is a widely used technique to identify the chemical components of a material under SEM. This method detects the X-rays produced as the result of the electron beam interactions with the sample.

These techniques allow improved understanding of the mechanism by which specific contaminants are bound in the matrix. For this study, the microstructure of OPC, ABW and its stabilized products were examined.

3.2.2 Particle Size Distribution

The grain-size distribution of the waste was divided according to the total mass of ABW into various fractions by particle size. The purpose of dividing the waste material into fractions of particle sizes is to determine the size distribution of the material. The sample is graded by vibrating stacked of sieves according to BS EN 933-1:2012, with the largest size of sieve at the top, for a specific time so that sample retained on each sieve represent the fraction coarser at the top and finer at the bottom. On the other extreme, wastes with a significant coarse fraction may require pre-screening to enable mixing equipment to operate and to preclude particle segregation. For this research, the sieve analysis was used to determine the size of ABW to be compared with the particle size of sand and also the particle size of coarse aggregates.

3.2.3 Specific Gravity

Specific gravity is a measure of the density of the sample solids relative to the density of water. The specific gravity of the abrasive blasting waste (ABW) and sand as fine aggregates were determined by using standard method of ASTM C128 – 15:2004 while the specific gravity of coarse aggregates were done as specified in ASTM-C127:2004. The test is related to the water absorption and density properties.

3.2.4 Water Absorption

If the ABW has high percentage of water absorption, then they are more porous in nature and generally considered unsuitable unless they are found to be acceptable based on their strength. The water absorption is determined by measuring the decrease in mass of a saturated and surface-dry sample after oven drying for 24 hours. The ratio of the decrease in mass to the mass of the dry sample, expressed as a percentage, is termed absorption (BS EN 1097-6: 2013). This test was also done to sand and coarse aggregates.

3.2.5 Density

The density test is considered to be a measure of strength or quality of the material (Shi *et al*., 2008). Thus, when waste is to be batch by volume, it is necessary to know the density which is the actual mass that would fill a container of unit volume, and this density is used to convert quantities by mass to quantities by volume. For the density test, pycnometer was used to determine the density of ABW.

3.2.6 Metal Analysis

The metal content in leachates before and after stabilization and solidification treatment was analysed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The instrument is equipped with computer software for data collection and sample processing. The operating conditions, instrument calibrations, emission measurement, wavelength selection and sample analysis followed the default conditions recommended by the manufacturer, Perkin Elmer.

A set of standards containing Ag, Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn was prepared for the calibration curves. Then, deionized water was used as blank solution to complete the calibration of the instrument. Next, samples were introduced in triplicate for analysis purpose. The blank solution was run in between sample analysis to prevent sample cross-contamination.

3.2.7 Normal Consistency of Cement

Normal consistency of cement test is a standard measure of plasticity of the cement paste. By using standard procedure from BS EN 197-1:2011 as a guide, a paste has a normal consistency when a Vicat plunger penetrates at 6±1 mm in 30 seconds. The apparatus must free of all vibrations during the test. New trial pastes with varying percentages of water were tested until the normal consistency of cement was obtained.

Selected freshly mixed ABW-cement paste samples were also tested for its consistency. The difference of the results will indicate ABW's contribution in the paste's consistency.

3.2.8 Setting Time of Cement

Selected freshly mixed samples were also tested for setting time. Setting time test is a test to find the time of initial set for cement paste, the time at which the cement paste can no longer be properly mixed or compacted. According to BS EN 196-3 (2016), the paste is at its initial setting time when the Vicat needle penetrates at 5±1 mm in 30 seconds. Final setting time of cement paste is the time required for the cement to harden to a point where it can sustain some load. This can be represented by zero penetration of the Vicat needle. The setting time is reckoned from the instant when water was added into the cement. Selected freshly mixed ABW-cement paste samples were also tested for its setting time. The difference of the results will indicate ABW's contribution in the paste's time to set with the same water-to-cement ratio.

3.3 Mix Design Study

The objective of the mix design study was to produce the optimum mix to satisfy the stabilization/solidification standard criteria which are maximum strength with minimum acceptable leaching discharge (US EPA, 1982b) (Sollars and Perry, 1989) that have the potential to be used as construction materials such as bricks and concrete.

Before promoting the potential usage of ABW as part of construction material, the experiment started by testing the possibility of stabilizing and solidifying ABW in cement paste. When the findings were satisfactory in terms of the compressive strength and leaching criteria, the second phase of the research work was to investigate the properties of bricks contained cement, ABW, sand and water. Both paste and brick were tested with different w/c ratio and percentage of ABW replacement. The ultimate compressive strength of the brick was then compared to the conventional clay bricks and sand-cement bricks. Once both main criteria of S/S were achieved, the bricks were tested for their engineering properties which include compressive strength, density and water absorption (BS 6073-2:2008).

After engineering bricks were successfully produced, further experiments were conducted to investigate the feasibility of ABW to be part of fine aggregates in making high strength concrete with targeted strength of at least 45 MPa (ACI, 1987). Figure 3.1 shows the laboratory tests planned for all sets of design mixes; cement-ABW paste, cement-ABW-sand brick and ABW concrete.

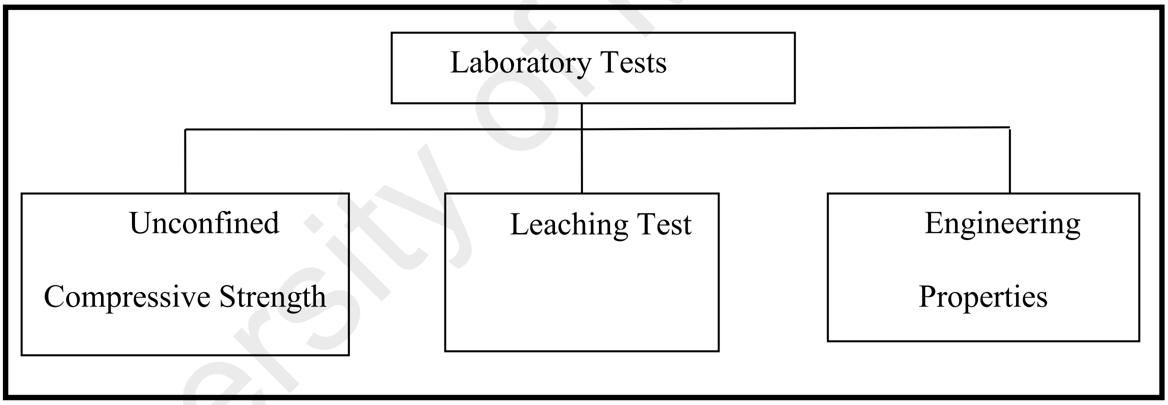

Figure 3.1: Flow Chart of Laboratory Tests for Engineering Brick and Concrete

3.3.1 Mix Design Control

The purpose of the trial mixes is to determine the workability and compressive strength of OPC mixes of various water-to-cement (w/c) ratios. Only a sufficient amount of water to produce the required workability of 5 to 7 mm penetration was used (BS EN 197-1:2011). From these trial runs, suitable w/c of optimum compressive strength was obtained as the mix proportion with different percentage by weight (wt. %) of abrasive blasting waste.

3.3.1.1 Mix Proportion of Cement/ABW paste

The mix proportion chosen for this study is given in Table 3.2. Cement/waste paste was designed with different ratio of cement to abrasive blasting waste ranging from 0.5 to 1.5. Five sets of cement/waste paste mixtures were prepared at 0.5, 0.75, 1.00, 1.25, and 1.5 c/ABW ratio. The amount of raw materials required in kg/m^3 were elaborated in the same Table to investigate the effect of binder-to-waste ratio to the solidified ABW. Control specimen (CCB), which do not contain the abrasive blasting waste, was also prepared.

Table 3.2: Mix Design of Solidified ABW

Specimen ID	C/ABW	Content of raw materials (kg/m^3)			w/c
		OPC	ABW	Water	
CCB	0	3307	0	992	0.30
				1158	0.35
				1323	0.40
				1488	0.45
				1654	0.50
C/ABW0.50	0.50	1180	2363	354	0.30
				413	0.35
				472	0.40
				531	0.45
				590	0.50
C/ABW0.75	0.75	1461	2051	438	0.30
				511	0.35
				584	0.40
				658	0.45
				731	0.50
C/ABW1.00	1.00	1698	1788	509	0.30
				594	0.35
				679	0.40
				764	0.45
				849	0.50
C/ABW1.25	1.25	1881	1585	564	0.30
				658	0.35
				752	0.40
				847	0.45
				941	0.50
C/ABW1.5	1.5	2027	1423	608	0.30
				709	0.35
				811	0.40
				912	0.45
				1013	1.50

3.3.1.2 Mix Proportion of ABW Bricks

Table 3.3 shows the mix design proportions of the cement-ABW brick. Ratio selected was 1:3 for cement: fine aggregates. W/c ratio for all the mixtures was fixed to 0.35. The ratio was found to be most suitable for mixing based on its workability during fresh stage.

Table 3.3: Mix Design of ABW Bricks

Specimen ID	ABW replacing sand (%)	Content of raw materials (kg/m^3)			w/c
		Cement	Sand	ABW	
0%CS	0%	420	1354	0	0.35
20%CS	20%	420	1063	266	0.35
40%CS	40%	420	797	532	0.35
60%CS	60%	420	532	797	0.35

3.3.1.3 Mix Proportion of ABW Concrete

To produce high strength concrete with minimum of 40 MPa compressive strength at 28th day of hardening, the design mix proportion selected is 1:1.63:2.92 for cement: fine aggregates: coarse aggregates with w/c of 0.65. The suggested sand replacement percentages were 20%, 40%, and 60%. The details of ABW concrete mix design are shown in Table 3.4. The method of calculation is shown in Appendix C.

Table 3.4: Mix Design of ABW Concrete

Specimen ID	ABW replacing sand (%)	Content of raw materials (kg/m^3)				w/c
		Cement	Sand	ABW	Gravel	
CCC	0%	300	519	0	913	0.65
C20	20%	300	415	104	913	0.65
C40	40%	300	311	207	913	0.65
C60	60%	300	207	311	913	0.65

The mix ratio of abrasive blasting waste, cement and aggregates for concrete production was determined based on previous research works for concrete design mix ratio done by Alnuaimi (2012), Brindha et al. (2010), Al-Jabri et al. (2011), Shi et al. (2008), Khanzadi and Behnood (2009) and Moura et al. (2007).

3.3.2 Preparation of S/S Waste for Tests

The constituents were prepared according to the chosen mix proportions discussed in Clause 3.3.1.1, Clause 3.3.1.2 and Clause 3.3.1.3. They were mixed in a clean and dry 25-litre capacity mixer from *Hobart*. ABW and OPC were first dry-mixed for homogeneity. Water was added last to avoid any early reaction to the mix. Mixing was performed for a total of 3 minutes from the addition of water in accordance to BS EN 196-1:2016.

Then, the fresh mixes were casted in different sizes of moulds, depending upon the types of experiment to be done. Table 3.5 shows the summary of specimen preparation.

Table 3.5 Specimen Count

Product test	Dimensions	Material	Unit	Reference
Paste blocks	50 mm cube	Perspex	3 x (1, 3, 7, 14, 28, 56 days)	ASTM (2005)
Leaching	25 mm cube	Perspex	3 x (1, 3, 7, 14, 28, 56 days)	ANSI (2003)
Bricks	215 mm × 102.5 mm × 65 mm	Perspex	3 x (1, 3, 7, 14, 28, 56 days)	BS EN 771-3 (2011)
Concrete UCS	150 mm cube	Steel	3 x (3, 7, 14, 28, 56 days)	BS EN 12390-3 (2009)
Concrete Tensile Splitting Test	150 Ø x 300mm cylinder	Steel	3 x 28th day	BS EN 12390-6
Concrete Flexural strength test	100 x 100 x 500 mm prism	Steel	3 x 28th day	BS EN 12390-5

25 mm x 25 mm x 25 mm Perspex moulds were for leaching procedure, while paste, brick and concrete mixes were prepared in 50 mm x 50 mm x 50 mm Perspex cube moulds, 215 mm × 102.5 mm × 65 mm Perspex brick moulds, and 150 mm x 150 mm x 150 mm steel concrete moulds respectively for compressive strength test, density test and water absorption test. The specimens were arranged in triplets for the UCS test which

were conducted at 1, 3, 7, 14, 28, and 56 days. There are also specimens casted in the prism and cylinder steel moulds for tensile splitting and flexural strength which will be tested on 28th day only. The casting was done in three layers. Each layer of the mixes were compacted by vibrating table for 30 seconds to yield a good packing. The specimen were air-cured at room temperature (25ºC to 33ºC) for 24 hours.

After 24 hours, the cubes were demoulded and put into a customized drying cabinet made of PVC and Perspex for further air curing. Air curing method was selected instead of water curing to avoid unnecessary leaching of the samples. The purpose of customizing the drying cabinet is to ensure a constant relative humidity and to reduce any air-borne dust deposition on the samples. The body of the cabinet is made of transparent Perspex for the better view of the samples from exterior while the perforated shelves are made of PVC. The bottom part of the cabinet is filled with water to ensure a constant relative humidity of ~90%. The doors were clamped tightly to minimize the loss of water due to evaporation.

3.4 Unconfined Compressive Strength Test (UCS)

Compressive strength is the capacity of material to withstand axially direct pressing forces. The behavior of material and its ability to resist under a crushing load can be observed under this test. In this study, the S/S specimens with various cement/ABW ratio were tested for UCS at the curing age of 1, 3, 7, 14, 28 and 56-days. Each sample was tested for UCS in triplicate and the average of the reading was recorded as the UCS for that particular sample.

The unconfined compressive strength (UCS) depends upon many of factors, which include the quality and percentage of the ingredient and the curing environment. The most important point of this test is the comparison of strength of the different ratio of solidified c/ABW paste, ABW bricks and concrete. The minimum w/c ratio of 0.30 is necessary to ensure that the water comes into contact with all the cement particles to ensure complete cement hydration. However, water/cement ratio range of 0.35 to 0.5 were chosen in order to achieve a workable consistency, so that fresh mixtures can be easily placed in the form. The strength increases due to the formation of Calcium Silicate Hydrate gel in the matrix. The strength of the mixtures is dependent upon the hydration reaction. Water plays a critical role, particularly the amount used. The strength of mixtures increased with decreasing water content. The hydration reaction itself consumes a specific amount of water.

3.5 Toxicity Characteristic Leaching Procedure (TCLP)

Crushed block leaching test was performed based on the US EPA Toxicity Characteristics Leaching Procedure (US EPA, 1986). In the TCLP test, waste samples were crushed to particle size of less than 9.5 mm and extracted with an acetate buffer solution with a pH of 5 or an acetic acid solution with a pH of 2.88 ± 0.05, depending on the alkalinity of the waste. However, the TCLP leachate is poorly buffered and that the pH of the leachate upon contact with the waste may be much greater, as high as pH 10 to11 or more, depending on the initial alkalinity of the waste. A liquid-to-solid ratio of 20:1 was used for an extraction period of 18 ± 2 hours. The leachate was filtered prior to conducting the contaminant analysis.

The filtered leachate was analyzed for toxic metal contaminant such as chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), and lead (Pb). Optima 3000 Perkin Elmer Inductive Coupled Plasma-Optical Emission Spectrometry (ICP-OES) was applied in this analysis.

This test is used to evaluate the leaching of metals, volatile and semi-volatile organic compounds, and pesticides from wastes that are categorized under Resource Conservation and Recovery Act (RCRA) as characteristically toxic and can be used on other waste as well.

3.6 Engineering Brick Tests

In BS 3921 (1985), engineering bricks are classified as A or B based on minimum compressive strength and maximum water absorption not falling below 70 N/mm^2 and 4.5% and 50 N/mm^2 and 7% respectively, as shown in Table 3.6. Hence, the designed S/S bricks must satisfy the following properties to be categorized as engineering brick.

Table 3.6: Properties of Engineering Brick

Element	Engineering Brick A	Engineering Brick B
Compressive Strength (N/mm^2)	≥ 70	≥ 50
Water Absorption (%)	≤4.5	≤7
Net dry Density (kg/m^3)	≥2200	≥2100

(Adapted from BS3921, 1985)

The test procedure of compressive strength, water absorption and density was described in Clause 3.4, Clause 3.2.4 and Clause 3.2.5 respectively.

3.7 Mechanical Test for Concrete

Five types of experiments were done to investigate the feasibility of using abrasive blasting waste (ABW) as fine aggregates in concrete. The tests are workability test, density test, compressive strength test, splitting tensile test, and flexural strength test.

3.7.1 Workability of Fresh Concrete

The test was performed using BS EN 12350-2: 2009. The test was only valid if it yielded a true slump, this being a slump in which the concrete remains substantially intact and symmetrical, and the true slump h was recorded to the nearest 10 mm. The targeted range of fresh concrete's workability for this research was in between of 25 mm to 75 mm slump. The correct range of workability will enhance the execution of works, resulting in less wastage and improved productivity.

3.7.2 Density Test

The objective of this test is to determine the density of test specimen hardened concrete. BS EN 12390-7:2009 was used as the reference for this test. The density of the test specimen is given by the equation:

$$D=mV$$

Where:

D is the density of the test specimen, in kg/m^3;

m is the mass of the specimen, in kg;

V is the volume of the specimen, in m^3.

The density was recorded to the nearest 10 kg/m^3.

3.7.3 Compressive Strength Test for Concrete

The compressive strength test was performed using BS EN 12390-3:2009, method for determination of compressive strength of concrete cubes. Compressive strength of the concrete is the maximum load a concrete can sustain under the crushing load, compressive strength is calculated by divining the maximum load by the original cross-sectional area of a specimen in compression test. The compressive strength is given by the equation:

$$f_c = F / A_c$$

Where:

f_c is the compressive strength, in MPa (N/mm^2);

F is the maximum load at failure, in N;

A_c is the cross-sectional area of the specimen on which the compressive force acts, calculated from the designated size of the specimen.

The compressive strength is to be expressed to the nearest 0.1 MPa (N/mm^2).

The results were determined from ELE (Engineering Laboratory Equipment) testing machine with load capacity of 2000 kN. The specimen were placed with the cast faces in contact with the platens of the testing machine and loading at the rate of 2.4 kN/s until failure. The test was conducted for the sample cubes on day 3, day 7, day 14 and day 28.

3.7.4 Splitting Tensile Test

The objective of this experiment is to determine the splitting tensile strength of hardened concrete test specimen. BS EN 12390-6 was used as the reference for this test. The tensile splitting strength is given by the equation:

$$fct = \frac{2 \text{ x F}}{L\ x\ d}$$

Where:

f_{ct} is the tensile splitting strength, in MPa (N/mm²);

F is the maximum load at failure, in N;

L is the length of the line of contact of the specimen, in mm;

d is the designated cross-sectional dimension, in mm.

The tensile splitting strength was recorded to the nearest 0.05 MPa (N/mm²).

3.7.5 Flexural Strength Test

The objective of this experiment is to determine the flexural strength of hardened concrete specimen. The standard used for this experiment is BS EN 12390-5.

The flexural strength is given by the equation:

$$f_d = (F \times I)/(d_1 \times d_2)$$

Where:

f_d is the flexural strength, in MPa (N/mm²);

F is the maximum load at failure, in N;

I is the distance between the supporting rollers, in mm;

d_1 and d_2 are the lateral dimensions of the specimen, in mm.

The flexural strength was recorded to the nearest 0.1 MPa (N/mm²).

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Analysis of Raw Materials

The raw constituents used in the preparation of the solidified waste forms were first analyzed for their properties.

4.1.1 Physical Properties and Heavy Metal Content of ABW

Scanning electron microscope (SEM), water absorption, density, and sieve tests were carried out in order to determine the physical properties of abrasive blasting waste (ABW) while leaching test were carried out to determine the heavy metal content of ABW. Table 4.1 shows the findings of the physical properties of ABW.

Table 4.1: Physical Properties of Abrasive Blasting Waste

Properties	**Findings**
Appearance	Shiny black, glassy, rough scratch surface
Particle shape	Angular, sharp, rough and colloidal
Density (kg/m^3)	2386
Water Absorption (%)	19.1
Specific Gravity	3.49
Fineness Modulus	3.47

4.1.1.1 Microstructure study of ABW

By general observation, the abrasive blasting wastes are majorly consists of black glassy copper slag with small amount of red exfoliated paint and brown flakes of corrosive metal. Figure 4.1 shows typical appearance of ABW collected.

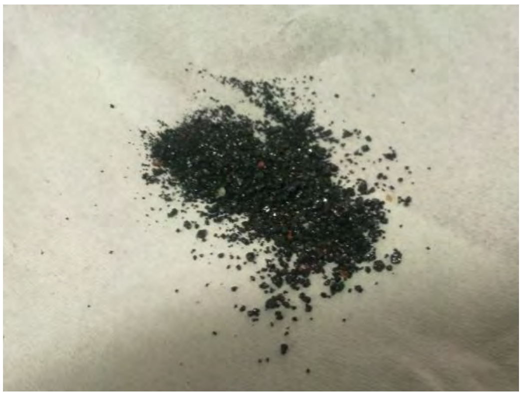

Figure 4.1: Abrasive Blasting Waste

The results obtained from the Scanning Electron Microscope (SEM) test demonstrate that the ABW particles are originally shiny black in colour. Figures 4.2(a), 4.2(b) and 4.2(c) show the abrasive blasting waste at different magnifications.

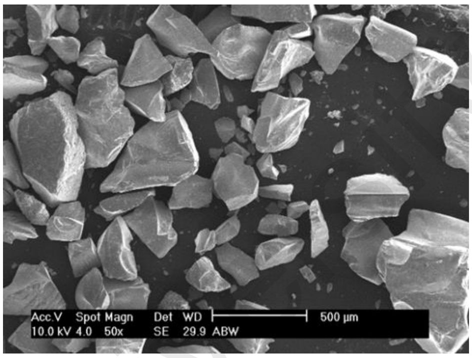

Figure 4.2(a): ABW at 50x magnification

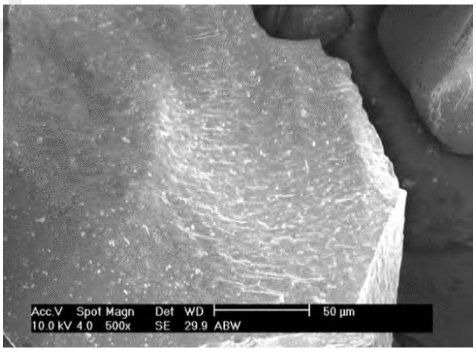

Figure 4.2(b): ABW at 500x magnification

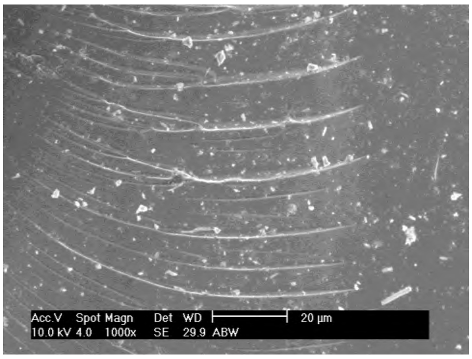

Figure 4.2(c): ABW at 1000x magnification

Figure 4.2(a) shows that the shape of the abrasive blasting waste particle at 50 times of magnification. The particle shapes were colloidal, sharp and angular, which are very good for interlocking with the cement paste. Figure 4.2(b) shows that at 500 times of magnification, ABW does not have obvious visible pores. This characteristic is line with its low water absorption behaviour. Then, at 1000 times magnification as shown in Figure 4.2(c), it is clearly seen that the particle have rough and scratched surface due to the repetitive blasting activities.

4.1.1.2 Porosity Analysis of ABW through BET

Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials. According to acquisition of isotherm plot shown in Figure 4.3, the result shows negative volume of first region whereby it is a sign that this sample consist of meso and macro porosities type with very shallow pore depth. Nevertheless, the depth are physically shallow due to inorganic metal blockage and this can be confirmed by SEM test for clear observation. After SEM test, it can be concluded that the abrasive blasting waste (ABW) has shallow pore depth.

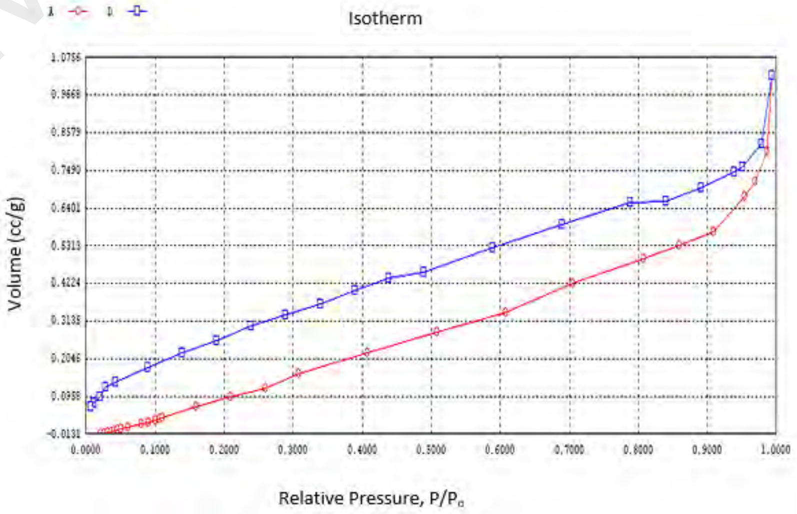

Figure 4.3: Porosity of abrasive blasting waste

4.1.1.3 Sieve Analysis of Abrasive Blasting Waste

Sieve test was carried out to determine the particle size distribution, fineness modulus and grading zone of the waste particle.

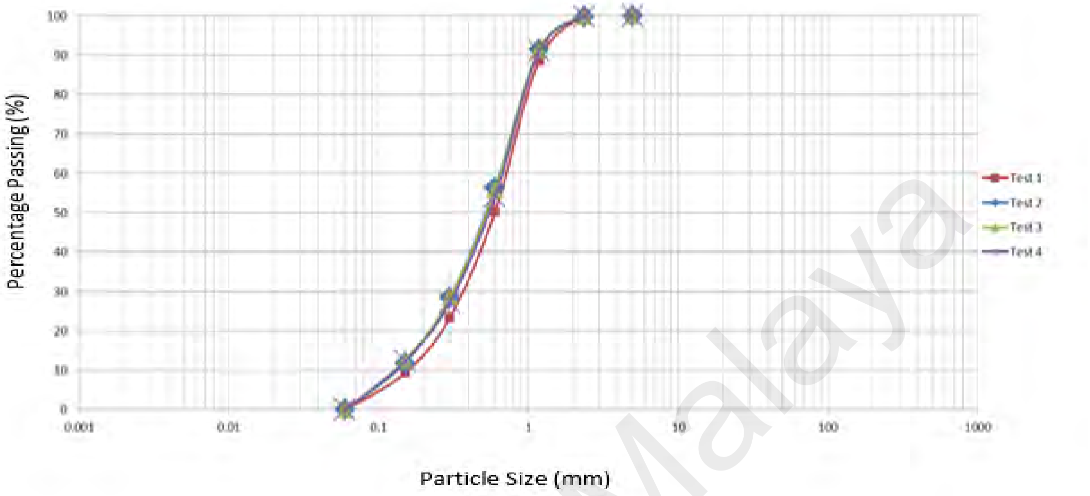

Figure 4.4: Graph of ABW Sieve Analysis

Figure 4.4 show the semi log graph of abrasive blasting waste particle sieve analysis. From the graph (lines are labelled as *Test 2, Test 3* and *Test 4* respectively), it was concluded that the abrasive blasting waste can be categorized as well graded particle as its effective size (d_{10}) was 0.146 mm, the uniform coefficient (Q_u) was greater than 5, and the coefficient of gradient (C_k) was within 0.5 and 2.0. This result also indicate that the ABW particle sizes was similar to the standard particle size of sand represented by the graph line labelled as *Test 1*. For this reason, the ABW is suggested to be explored as sand replacement material for this research during the production of bricks and concrete

4.1.1.4 Water Absorption

The water absorption test was conducted based on BS EN 1097-6: 2013 to determine the moisture content of ABW as a percentage of its dry weight. The sample was weighed, dried in an oven, and then reweighed under standard conditions. After three tests, it was found out that the water absorption results varied between 18.4% to 19.6%. The result was comparable to Shi *et al.* (2008) and Lim and Chu (2006). The researchers have reported that the water absorption of spent copper slag was 17.5% and 18.0% respectively.

4.1.1.5 Leaching of Heavy Elements in Abrasive Blasting Waste

Two methods were used to identify the chemical contents of the abrasive blasting waste before the treatment as discussed below:

(a) Energy dispersive x-ray analysis (EDAX)

Figure 4.5 shows a significant amount of carbon, silica and oxygen in the abrasive blasting waste sample. There were also small peaks of Fe, Al, Mg and Zn detected in the sample. However, EDAX was not able to detect copper (Cu) which is the major component of the ABW sample. Hence, test on the chemical content was also done using ICP-OES.

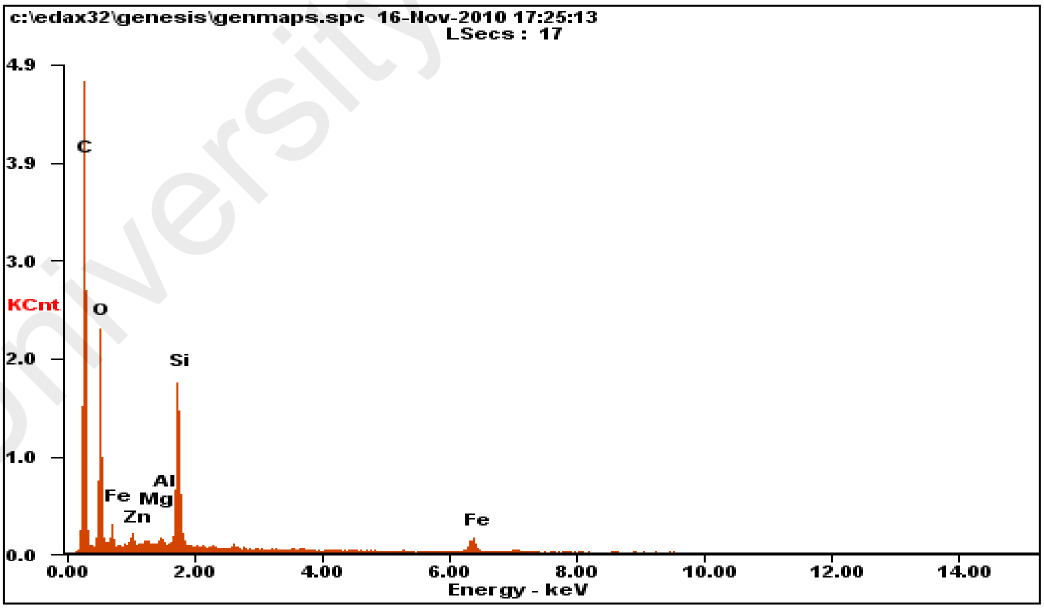

Figure 4.5: Chemical components of ABW by EDAX

(b) *Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)*

Abrasive blasting waste (ABW) was also analyzed for its heavy metal element using ICP techniques. The metal wastes were dipped in distilled water up to 15 days according to standard method of ASTM D5233 that provide an indication of the leaching potential involving samples of untreated waste. Table 4.2 presented the leaching result of heavy metals constituents of the abrasive blasting waste.

Table 4.2: Heavy Metal of Abrasive Blasting Waste

PARAMETER	CONCENTRATION (mg/kg)	DOE (1989) REGULATION GUIDELINE LIMIT (mg/kg)
Arsenic, As	342	500
Barium, Ba	848	10,000
Cadmium, Cd	15	100
Chromium, Cr	466	2500
Copper, Cu	<u>9932</u>	2500
Nickel, Ni	107	2000
Plumbum, Pb	909	1000
Vanadium, V	57	2400
Zinc, Zn	<u>110467</u>	5000

Comparison was made with Malaysia Department of Environment Regulation Guideline Limit (DOE, 1989). It was observed that out of the ten elements, two elements; Copper and Zinc exceeded the allowable limit. Hence, the abrasive blasting waste need to be treated to reduce the concentration of these two elements.

4.1.2 Properties of Ordinary Portland Cement

Ordinary Portland Cement (OPC) were tested for its consistency and initial setting time to be the control of other design mixes later.

4.1.2.1 Normal Consistency of Ordinary Portland Cement

Based on the consistency test for Portland cement conducted according to BS EN 197-1 (2011), the optimum percentage of water required was 40% of total cement weight. The result was used as a guideline to select the range of w/c for designing the mixtures to produce bricks and concrete.

4.1.2.2 Initial Setting Time of Ordinary Portland Cement

The initial setting time of OPC, determined in accordance with BS EN 196-3 (2016) shall not be less than 60 minutes. The time needed for the Vicat needle to penetrate the sample block by 5.0 ± 1 mm from the bottom of the mould has been observed to be 92 minutes.

4.1.3 Physical Properties of Aggregates

The fine aggregates used in this study was mining sand, which is a common type of sand used in building and infrastructure construction in Malaysia especially for materials like bricks and concrete. Coarse aggregates used in this research was crushed granite, which is also easily available in Malaysia.

The physical properties of aggregates that are important to know are the specific gravity, particle size distribution, moisture content and water absorption. Table 4.3 shows the physical properties of the aggregates used in this research.

Table 4.3: The physical properties of fine and coarse aggregates

Aggregate	**Water Absorption (%)**	**Specific Gravity**	**Particle Size (mm)**
Mining sand	1.08	2.67	0-4.75
Crushed granite	0.65	2.5	4.75-19

4.2 Cement/Abrasive Blasting Waste (ABW) Paste Test Results

The result findings of ABW paste were extensively discussed in Section 4.2.1 for its consistency and initial setting time, Section 4.2.2 for its unconfined compressive strength, Section 4.2.3 for its toxicity leaching characteristics and Section 4.2.4 for its solidified and stabilized microstructures.

4.2.1 Consistency and Setting Time of Cement/ABW Paste

The consistency and setting time of ABW paste was done based on BS EN 197-1 (2011). Table 4.4 shows the findings of the experiment.

Table 4.4 Consistency and Setting Time of ABW Paste

Experiment	Cement Paste	ABW/ Cement 1.25 Paste
Consistency	0.40	0.32
Setting Time	92 minutes	78 minutes

When there is no content of ABW, the amount of water required is 40% of the cement's weight with initial setting time of 92 minutes. However, when ABW was mixed with cement, the consistency of the mix is 32% with 78 minutes of initial setting time.

If the consistency of ABW/Cement 1.25 is fixed at 40%, the initial setting time of the paste was found to be 120 minutes. Hence, these findings prove that ABW retards the setting time of cement paste.

4.2.2 Unconfined Compressive Strength (UCS) for Cement/ABW Paste

The result findings of unconfined compressive strength for ABW paste were elaborated in Section 4.2.2.1 for the w/c ratio effect on control samples, Section 4.2.2.2 for its w/c ratio effect on different c/ABW design mixes, and Section 4.2.2.3 for the cement/ABW paste ratio effect towards the compressive strength.

4.2.2.1 Water/Cement Ratio Effect on Control Samples

The UCS test was performed on the cement paste with ABW at the age of 1, 3, 7, 14, 28 and 56 days. Figure 4.6 shows the compressive strength of the C/ABW control samples with different w/c ratios. The optimum strength was achieved with the lowest w/c content of 0.30. However, due to poor workability of this mix, w/c content of 0.35 was chosen to be used during the design mix of the bricks. Details of UCS results of control paste are given in Appendix G.

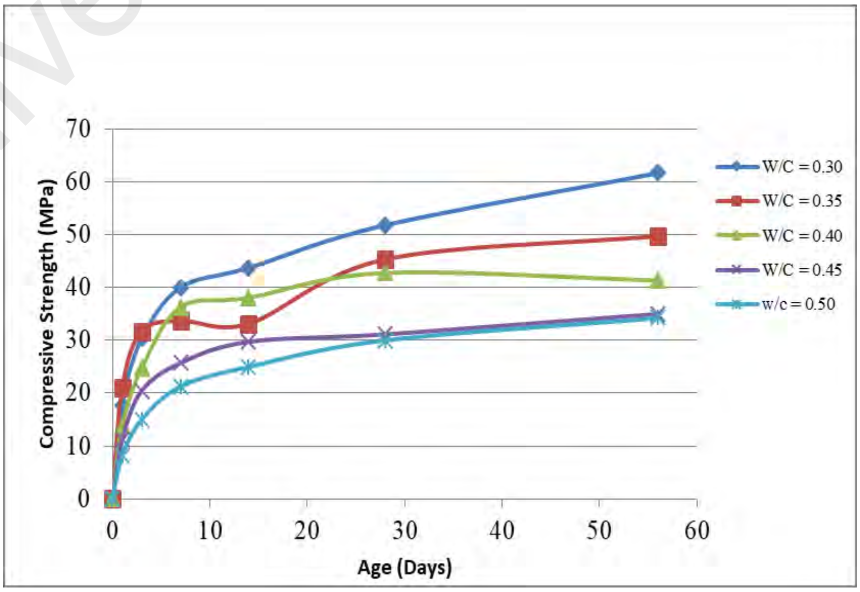

Figure 4.6: Compressive Strength of C/ABW Control Paste

4.2.2.2 Water/Cement Ratio Effect on Different c/ABW Mixes

All the results showed similar pattern although four different c/ABW mix were used. The graphs of water-to-cement ratio comparison for different c/ABW mix are given in Figure 4.7, Figure 4.8, Figure 4.9 and Figure 4.10.

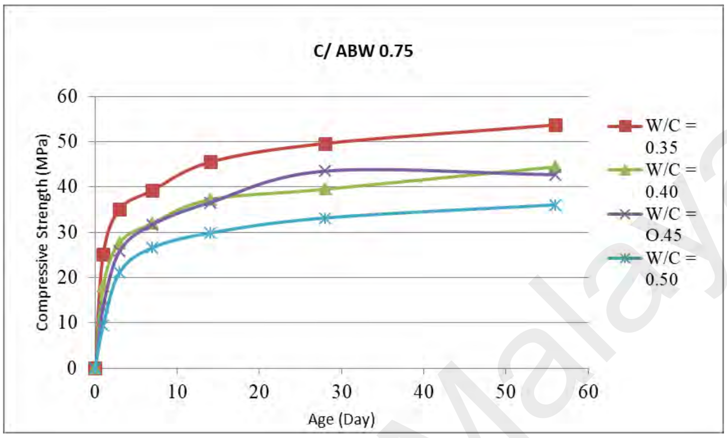

Figure 4.7: Compressive Strength of C/ABW 0.75 Paste

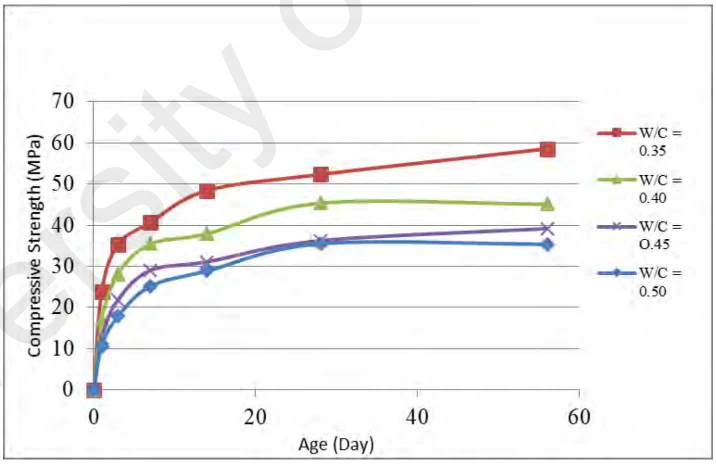

Figure 4.8: Compressive Strength of C/ABW 1.00 Paste

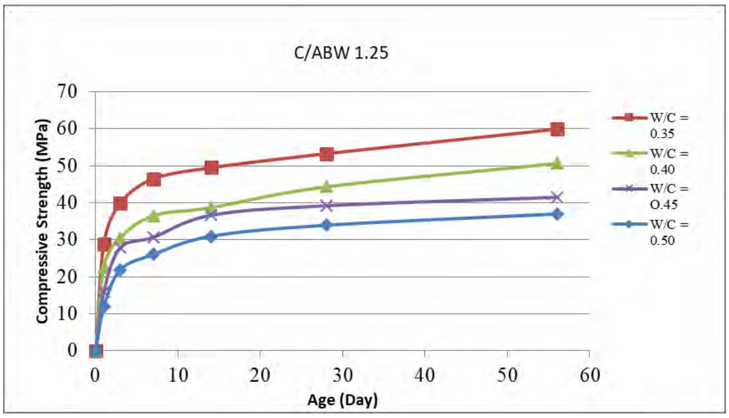

Figure 4.9: Compressive Strength of C/ABW 1.25 Paste

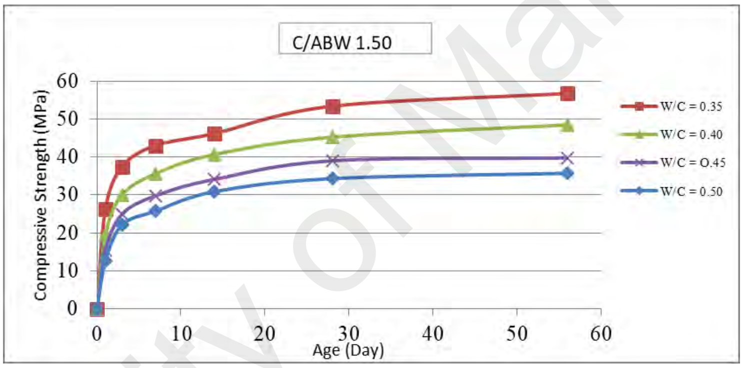

Figure 4.10: Compressive Strength of C/ABW 1.50 Paste

In waste solidification processes the w/c ratio must be kept as low in order to obtain a low permeability waste forms. At very high w/c ratio, segregation of mix constituent may occur before set is achieved. Since Portland cement is categorized as hydraulic cement, it will continue to set under segregate water or 'bleed water'. However, the presence of permanent bleed water in the solidification process is undesirable because is it not only mobile but contains the soluble waste contaminants. Hence, it decided that w/c of 0.35 will be used in the ABW bricks design mix.

From the graphs shown in Figure 4.7 to Figure 4.10, the compressive strength of paste decreased with higher w/c ratio, causing reduction in the strength. High water content in the mix causes the particles of the constituents to separate, leaving pores in the hardened concrete which consequently reducing the strength (Al-Jabri, 2006).

However, the compressive strength of all mixes were found to be higher than the control paste. As an example, 28th day compressive strength of C/ABW 0.75, 1.00, 1.25 and 1.5 at w/c ratio of 0.35 are 49.6 MPa, 52.31 MPa, 53.3 MPa and 53.37 MPa respectively compared with control paste with 28th day of compressive strength of 45.3 MPa. The compressive strength was also found to increase with increasing ratio of ABW, due to ABW's stiffer property.

Even though the initial setting time of ABW paste is slower than control paste, it was observed that fast strength development occurred during hardening stage for the ABW paste mixes as shown in Figures above, with up to 90% strength achieved on day-7 for w/c ratio of 0.35. The retardation is due to the inference mechanism of metal content in ABW.

As no researchers has explored the possibility of using S/S method in treating the ABW, the comparison of results were done with other researchers who explored the utilization of similar waste, copper slag as cement mortar. Nazer et al. (2012) reported that the 28th day compressive strength of the mortar using 100% copper slag is 44% higher than the values achieved in mortars using river sand. Reddy *et al.* (2016) stated that there was more than 21% improvement in the compressive strength of cement mortars with 40% copper slag substitution in comparison with the control mixture (i.e. 100% sand) at 28 days of curing. Salleh and Dayanand (2016) also found similar pattern of results. The compressive strength of the mortar specimens has increased when a percentage of 35% to 40% of copper slag was added by proportionally reducing the amount of sand. However when 50% of copper slag was added to the mortar mix; the compressive strength decreases slightly but it was still higher than the conventional mortar. These findings justify the results observed in this research.

4.2.2.3 Cement/ABW Paste Ratio

The highest compressive strength value recorded for cement/ABW paste at 28 days was 53.4 N/mm^2 from C/ABW of 1.25 ratio specimen with w/c 0.35. Figure 4.11 shows the UCS comparison of different C/ABW ratio with water-to-cement ratio of 0.35.

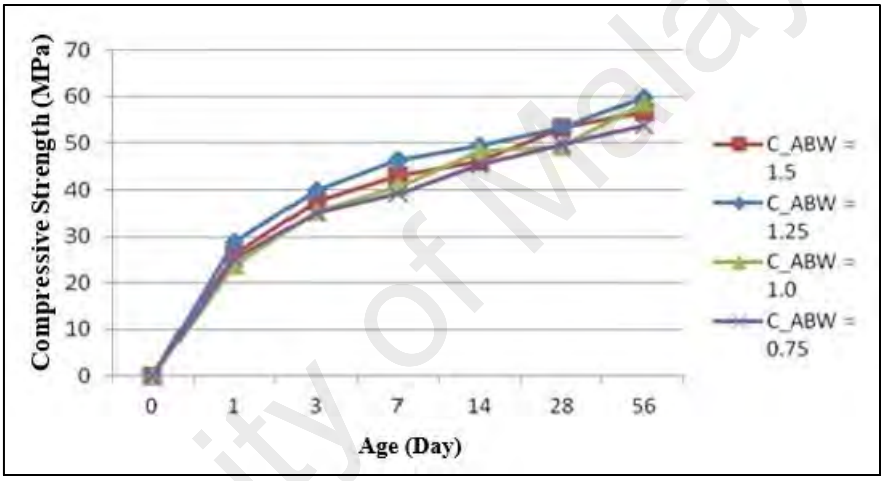

Figure 4.11: UCS of different C/ABW ratio specimens at W/C 0.35

The graph also showed that the strength development of the solidified C/ABW paste keep increasing even at 56th day.

All the mixes showed the same trend of strength development. Mixes with lower w/c ratio gave higher compressive strength. Higher cement/ABW ratio mixes were able to resist higher loads. Due to the higher amount of cement in the mix, the interbonding between the cement and ABW particles become stronger. Details of UCS results of ABW paste are given in Appendix H.

The first criteria of cement solidification and stabilization method which is compressive strength of encapsulated waste shall be more than 0.34 N/mm^2 was achieved.

4.2.3 Toxicity Characteristic Leaching Procedure Results for C/ABW Paste

In this experiment, the concentration of multi element of metal in the solidified C/ABW brick has been tested by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The metal elements tested were Al, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn. The results for the metal concentrations detection in the C/ABW bricks with 0.35 w/c is shown in Table 4.5.

Table 4.5: Metals Concentration of C/ABW paste at W/C 0.35 at 28 days

Element	**Metal Concentration (mg/L)**					
	C/ABW 0.75	C/ABW 1.0	C/ABW 1.25	C/ABW 1.5	Sollars and Perry (1989)	Kualiti Alam (2001)
Al	0.795	0.436	0.531	0.481		
Cd	0.240	0.139	0.108	0.108	5	1
Cr	0.613	0.165	0.185	0.193	5	5
Cu	0.328	0.037	0.078	0.066	5	100
Fe	0.307	0.139	0.116	0.110		
Mg	0.352	0.124	0.149	0.147		
Mn	0.307	0.104	0.133	0.133		
Ni	0.239	0.130	0.110	0.051	5	100
Pb	0.234	0.098	0.092	0.067	5	5
Zn	0.307	0.078	0.090	0.086	10	

From the results shown in Figure 4.12, it shows that the metals released in the TCLP extracts were very low. This indicated that the concentration of the metal element in the TCLP extract was reduced significantly using the S/S technique. Hence, the second criteria of cement solidification and stabilization method which is the leaching concentrations of metals in all the C/ABW paste specimens were lower than the U.S. EPA toxicity regulatory level (US EPA, 1990) and Malaysia DOE regulatory level guideline (DOE, 1989) was fulfilled (Kualiti Alam, 2001). TCLP results for all samples are listed in Appendix I.

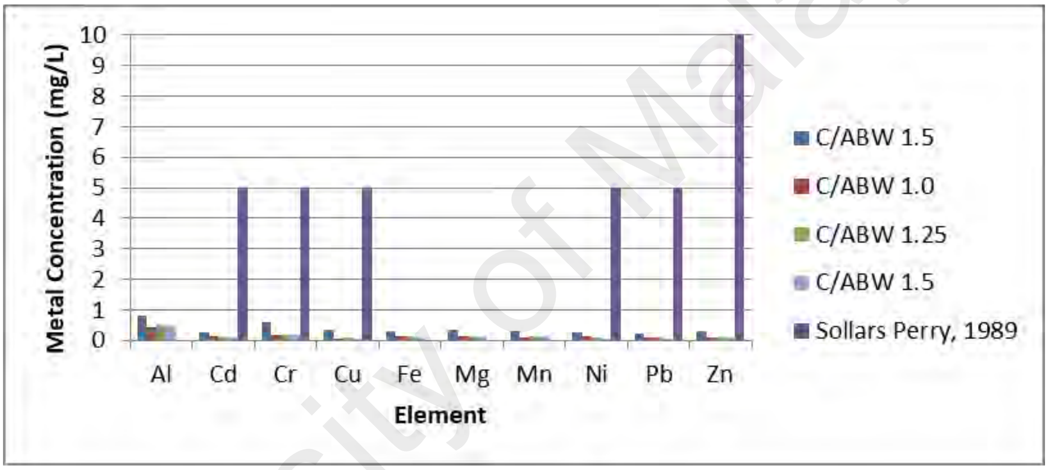

Figure 4.12: Metals Concentration of C/ABW paste at W/C 0.35

After both criteria of compressive strength and leachability levels were satisfied, the treated abrasive blasting waste was explored as construction materials e.g. bricks and concrete, to enhance the utilization of the waste instead of disposing the S/S product to landfill.

4.2.4 Microstructure of Solidified Cement-ABW Paste

The structural development of solidified cement paste is a result of complex hydration reaction that stiffens, densify and impart structural integrity on the product (Conner, 1990). The main hydration phases under normal conditions are C-S-H gel of variable stoichiometry and calcium hydroxide which together form about 90 % (w/w) of the solid hydration products in an OPC paste. The other solid hydration products are hexacalcium aluminoferrite trisulfate or “ettringite” type phases and tetracalcium aluminate monosulfate or “monosulfate”.

In this research, the microstructural development of the waste forms was studied using Scanning Electron Microscope (SEM). The SEM micrographs of the solid raw materials used in the mix formulation and solidified ABW paste are presented in Figure 4.14 and Figure 4.15 respectively.

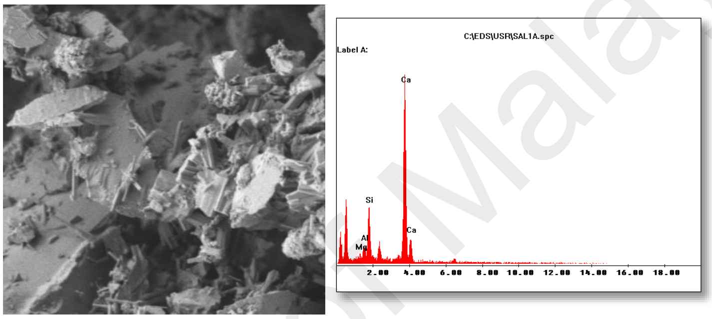

Figure 4.13: Cement Paste as Control

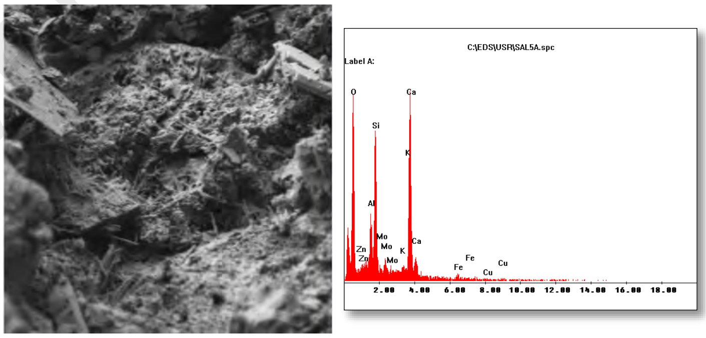

Figure 4.14: Solidifed C/ABW

All photomicrographs of C/ABW were captured at 10,000 times. The main element in the solidified ABW was calcium distributed in cement product of CH, C-S-H and ettringite.

Silica content was increased with the inclusion of ABW compared to the solidified OPC alone. The hydrated products of solidified c/ABW have indicated less ettringite distribution. Solidified cement as control paste has finer and smoother surface compared to C/ABW paste which contains more voids on its surface.

The incorporation of ABW retards the setting time of cement hydration due to excessive metal content. The ABW has increase densification and durability, reduce bleeding and increase ultimate strength of the paste (Glasser, 1993, Taylor, 1990, Lea 1970, and Portland Cement Association, 2001).

4.3 Abrasive Blasting Waste (ABW) Bricks

The result findings of ABW bricks were discussed in Section 4.3.1 for its density, Section 4.3.2 for its water absorption, and Section 4.3.3 for its unconfined compressive strength. While in Section 4.3.4, comparison of ABW brick's properties with other conventional bricks and engineering bricks were done.

4.3.1 Density of ABW Bricks

Table 4.6 shows the increase in the density of all the samples tested after 28 day. The optimum value was obtained at the 60% replacement of fine sand with ABW with the density of 2353 kg/m^3 compared to the control sample which has zero percentage of ABW with the density value of 2075 kg/m^3.

Table 4.6 Density of ABW Bricks after 28 Days

Specimen ID	ABW replacing sand (%)	Average Density (kg/m^3)	Engineering Brick B (BS3921)
0%CS	0% (Control)	2075	>2100 kg/m^3
20%CS	20%	2225	
40%CS	40%	2329	
60%CS	60%	2353	

The density of cement sand brick was increased by almost 14% for mixture of 60% ABW replacement as fine aggregates, which is due to the characteristic of ABW's high specific gravity compared with fine aggregates. Hence, the higher the percentage of ABW ratio in mixtures, the higher the density of ABW bricks. All the ABW bricks samples fulfilled the requirement of Engineering Brick B's density which is more than 2100 kg/mm^3 (BS3921).

4.3.2 Water Absorption of ABW Bricks

Results in Table 4.6 indicated that the water absorption of ABW bricks with w/c ratio tested at 28 day fulfilled the requirement of Engineering Brick B which is less than 7% (BS3921).

Table 4.7: Water Absorption of ABW Bricks at 28th Day

Brick Specimen	Percentage of Water Absorption	Engineering Brick B (BS3921)
0%CS	4.92 %	< 7%
20%CS	6.35 %	
40%CS	6.15 %	
60%CS	4.55 %	

Mahendran *et al* (2017) concluded that the water absorption of brick become poor in large proportion of copper slag as substitute of red soil in raw material mixtures of bricks. The range of water absorption recorded by Mahendran *et al* (2017) are from 5% to 20%, depending on the percentage of substitution.

4.3.3 Unconfined Compressive Strength of ABW Bricks

The experiment was done in accordance to BS EN 12390-3:2009. Table 4.8 shows the compressive strength findings for hardened samples containing 20%, 40% and 60% of sand weight replaced by abrasive blasting waste.

Table 4.8: Compressive Strength for different proportions of ABW bricks

Specimen	Compressive strength (MPa)					
	1 day	3 day	7 day	14 day	28 day	56 day
0%CS	0	19.1	30.8	37.1	43.2	45.3
20%CS	0	26.9	37.0	43.4	50.0	65.3
40%CS	0	28	31.8	38.1	40.1	45.2
60%CS	0	22	27.4	33.9	34.2	38.5

The compressive strength of the brick decreases when the amount of ABW increases. It was also observed that 1-day compressive strength results for all mixes are 0 MPa due to retardation effect. 20% of ABW bricks (labelled as 20%CS) achieved the compressive strength of engineering brick Class B compared to the minimum specific cement sand brick strength of 5 N/mm^2. Figure 4.15 shows the maximum strength achieved was at 28th day with 50 N/mm^2. Hence, the optimum compressive strength of the mix is at 20% fine aggregates replacement. Higher replacement will retard the strength development due to interference mechanism between ABW and OPC.

According to BS 3921:1985, the Class B engineering bricks shall have the strength more than or equal to 50 N/mm^2.

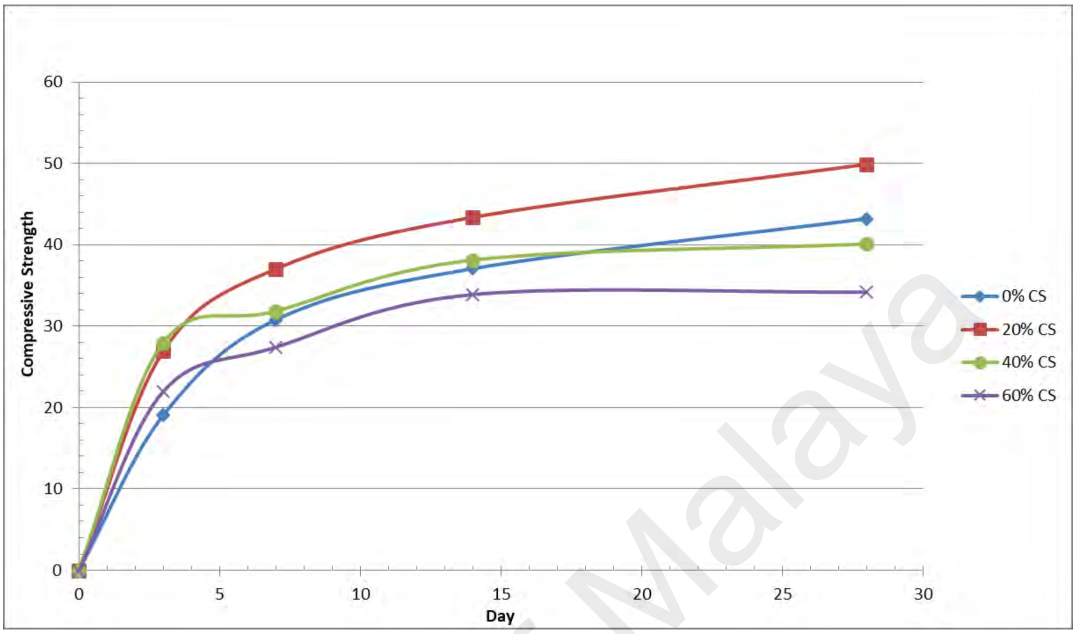

Figure 4.15: Compressive Strength for different proportions of ABW bricks

4.3.4 Comparison of UCS with other Bricks

The compressive strength of ABW bricks were compared with two types of conventional bricks; clay brick and calcium-silicate bricks. Table 4.9 shows the dimensions of the conventional bricks while Table 4.10 gives the results of their compressive strength.

Table 4.9: Dimensions of Conventional Brick Samples

Sample	Height (mm)	Width (mm)	Length (mm)
Clay brick 1	70	100	225
Clay brick 2	68	103	220
Clay brick 3	70	102	220
Calcium-silicate brick 1	67	100.5	217
Calcium-silicate brick 2	66	102	218
Calcium-silicate brick 3	65	101.5	216.5

The compressive strength of 20%CS brick at 28th day is 87.26% and 87.5% stronger than the clay brick and calcium-silicate samples respectively. Due to its high strength, it may be categorized as Engineering Brick Type B (BS3921).

Table 4.10: Compressive Strength of Conventional Brick Samples

Brick Sample	Density (kg/m^3)	Compressive Strength at 28 day (N/mm²)	Average Compressive Strength at 28 day (N/mm²)
Clay brick 1	1641	7.1	6.80
Clay brick 2	1641	7.1	
Clay brick 3	1710	6.2	
Calcium-Silicate 1	1920	5.0	6.7
Calcium-silicate 2	1815	3.6	
Calcium-silicate 3	1920	11.4	
20%CS	2225	50.0	50.0
Engineering Brick Type B (BS3921)			≥50.0

Comparison of compressive strength was also done with other published research findings on similar waste, copper slag. Mahendran *et al.* (2017) reviewed the potential of recycling various waste like copper and rice husk ash (RHA) in bricks production as partial replacement of red soil in raw material mixtures. The article reported that the compressive strength of these bricks varies from 3.6 N/mm^2 to 4.8 N/mm^2. Kanagalakshmi *et al.* (2015) evaluate the technical possibilities of incorporating fly ash, copper slag, marble dust and gypsum in the construction bricks. The compressive strength is within the range of 6.9 N/mm^2 to7.3 N/mm^2. Their compressive strength a much lower than ABW bricks, which are not suitable to be categorized as Engineering Bricks. No research found regarding utilization of copper slag in the production of Engineering Bricks. One of the current engineering bricks in market is Wienerberger Engineering Brick with compressive strength of 75 N/mm^2 (Wienerberger, 2018).

4.4 Abrasive Blasting Waste (ABW) Concrete

The result findings of ABW concrete were discussed in Section 4.4.1 for its workability, Section 4.4.2 for its density, Section 4.4.3 for its unconfined compressive strength, Section 4.4.4 for its splitting tensile strength and Section 4.4.5 for its flexural tensile strength.

4.4.1 Workability of Fresh ABW Concrete

Workability of fresh concrete can be defined as one which can easily be transported, placed and consolidated without segregation or excessive bleeding (Afiniwala et al., 2013). Slump test is the common test used in concrete industry to check or to control the workability of fresh concrete (Tam, 2003). To find the effect of ABW towards the workability of fresh concrete, slump test was conducted on concrete mixes for different percentage of replacement of ABW for fine aggregate and the results are shown in Table 4.11. The test was done according to BS EN 12350-2 (2009) requirements.

Table 4.11: Slump Value

Batch ID	Mixture	w/c	Slump Value (mm)
C0	0% ABW (Control)	0.65	40
C20	20% ABW	0.65	45
C40	40% ABW	0.65	55
C60	60% ABW	0.65	70

In the process of producing high strength concrete, a controlled mixture named as Batch C0 had to be made as benchmark for other findings. This mixture was produced with a w/c of 0.65. The slump value is 40 mm which is within the required range of 25 mm to 75 mm (BS EN 12350-2:2009). Batch C0 was properly mix and well compacted during placing. Hence, no honeycomb was found on the specimen of Batch C0 mix.

Batch C20 was produced using all basic constituents of concrete except 20% of sand was replaced by ABW by weight. ABW was expected to play a big role in increasing the strength of concrete. Past researches showed that 20% replacement of sand by copper slag gave the optimum strength for high strength concrete, but none researched on the optimum amount of ABW that gave the highest strength to concrete. The w/c used in this batch was maintained as 0.65. However, slump value shown in Table 4.9 shows a slight increase for Batch C20 compared to Batch C0.

The addition of ABW was then increased to 40% of sand volume for Batch C40. The w/c was maintained to 0.65. The workability of the concrete was good with slump value of 55 mm.

Batch C60 with 60% replacement of sand volume by ABW was produced with a w/c of 0.65. This batch was made to check whether the 60% ABW replacement could increase the strength more than that of Batch C20 or Batch C40. The w/c was not changed to fix the variable. The slump value for Batch C60 was 70 mm which is highest among the mixes.

The workability of the mixes are high due to heavier specific gravity of the ABW, and not due to water absorption. Hence, the higher the percentage of replacement, the higher the slump. This is in agreement with findings by Shi et al (2008) and Lim and Chu (2006).

4.4.2 Density of ABW Concrete

Table 4.12 shows the increase in the density of all the samples tested after 28 day. The addition of ABW as a partial replacement of fine aggregates has also increased the density of the concrete. The optimum value was obtain at the 60% replacement of fine sand with

ABW with the density of 2333.3 N/mm^3 compared to the control sample which has zero percentage of ABW with the density value of 2283.5 N/mm^3.

Table 4.12 Density of ABW Concrete after 28 Days

Batch ID	Mixture	Average Density (N/mm^3)
C0	0% ABW (Control)	2283.5
C20	20% ABW	2303.4
C40	40% ABW	2319.4
C60	60% ABW	2333.3

The increase of ABW concrete density is contributed by high specific gravity of abrasive blasting waste of 3.49 compared to fine aggregate which has specific gravity of 2.67. The result is aligned with findings from Tamil Selvi *et al* (2014) and Al Jabri (2006). Tamil Selvi *et al* (2014) reported that the density of concrete with copper slag as partial replacement of fine aggregates increased mainly due to the higher specific gravity of copper slag which was 3.45 compared with sand which has a specific gravity of 2.47. She also added that addition of copper slag definitely reduced the pores of concrete and made the concrete impermeable. Meanwhile, Al Jabri (2006) recorded the specific gravity of copper slag utilized in concrete mix as 3.4 compared to fine aggregates which has specific gravity of 2.8, which contributes to the increase of concrete density.

4.4.3 Compressive Strength of ABW Concrete

The development of compressive strength over 28 days for all concrete design mixes is shown in Figure 4.16. The compressive strength of the control sample (C0) at day 28 was 45.53 N/mm^2, while the compressive strength obtained for the concrete containing 20% of sand weight replaced by ABW was 79.33 N/mm^2, for 40% replacement, compressive strength is 59.87 N/mm^2 and for 40 % the replacement the compressive strength is 45.70 N/mm^2 after 28 days of air curing. The strength of samples containing abrasive blasting waste (ABW) indicated a high strength when compared with the control samples. The optimum strength was obtained with a mix of 20% ABW replacement at 79.33 N/mm^2.

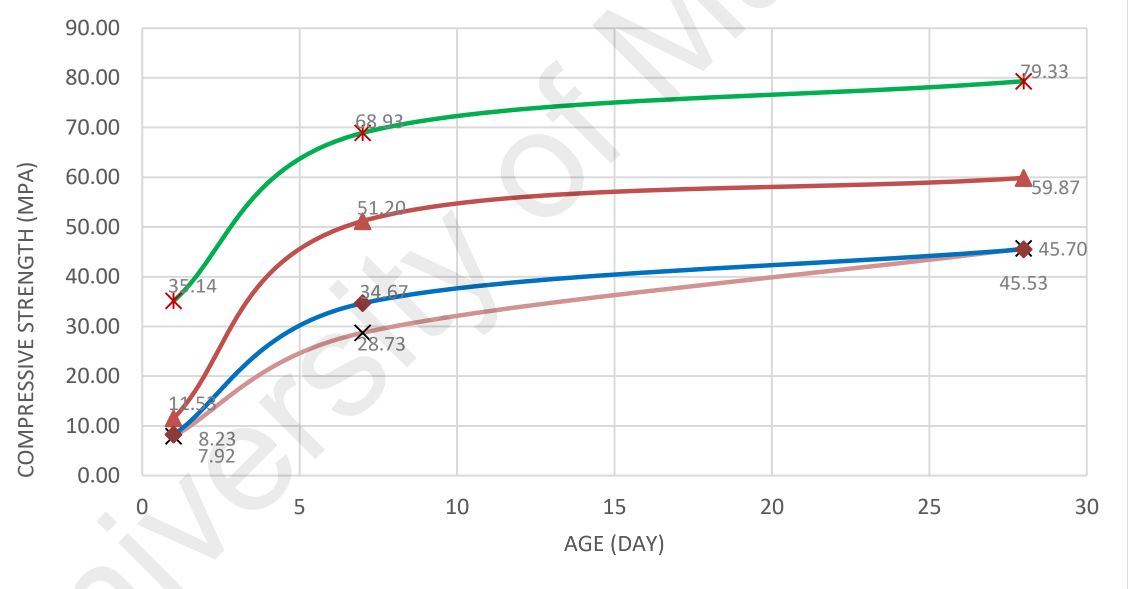

Figure 4.16: Development of Compressive Strength over 28 days for all Concrete Design Mixes

The result is aligned with findings from Honnakkalavar *et al.* (2018) and Al Jabri (2006). Honnakkalavar *et al.* (2018) investigated the effect of concrete strength when copper slag is added at varying percentages of 0%, 20%, 40%, 60% and 80% by replacing fine aggregate. The research reported that there are increase of compressive strength with the increase of copper slag percentage up to 40% CS replacement. The compressive strength of 40% replacement of fine aggregate by copper slag for 28 days is 32.4 N/mm^2 and for 7 days is 30.52 N/mm^2 is higher as compared to conventional mix that are 25

N/mm^2 and 26.64 N/mm^2 for 7 days and 28 days respectively. However, the compressive strength drops at 60% and 80% CS replacement. Meanwhile, Al Jabri (2006) mentioned that the compressive strength of concrete is generally increases as copper slag quantity increases up to 20% sand replacement. The highest 28th day compressive strength was 95.3 MPa for 20% CS mix compared with 93.9 MPa for the control mix, while 40% CS mix gave 28th day compressive strength of 79.6 MPa and 80% CS mix with compressive strength of 79.0 MPa. The compressive strength is slightly decreased due to the significant increase in the workability causing reduction in the strength. High water content in the mix causes the particles of the constituents to separate leaving pores in the hardened concrete which consequently reducing the strength. Adding to this statement, Alnuaimi (2012) concluded that although the concrete density increases due to the increase in CS content, the porosity also increases, which adversely effects the concrete strength.

4.4.4 Splitting Tensile Strength of ABW Concrete

The splitting tensile strength test results for the 20%, 40% and 60% ABW replacement were 2.29 MPa, 1.87 MPa, and 1.73 MPa respectively as shown in Figure 4.17. The splitting tensile strength for the CC mix was 2.09 MPa. It can be observed from these results that the splitting strength is directly proportional to its compressive strength and that the 20% ABW replacement concrete has higher splitting tensile strength than the CC mix. The splitting tensile strength was also noted to decrease when the percentage of ABW replacement increases.

4.4.5 Flexural Tensile Strength of ABW Concrete

The results for the flexural tensile test is shown in Figure 4.17 below. The flexural tensile strength test results for the 20%, 40% and 60% ABW replacement were 3.71 MPa, 3.17 MPa and 2.97 MPa respectively. The flexural tensile strength for the CC mix was 4.12 MPa. It can be observed from these results that the flexural strength decreases when percentage of ABW replacement is increased. The CC mix was recorded to have greater flexural strength than the ABW mixes, this might be due to the better stiffness and strength of granite as aggregate compared to ABW. Hence, the optimum mix to reach the highest flexural tensile strength is at 20% CS replacement.

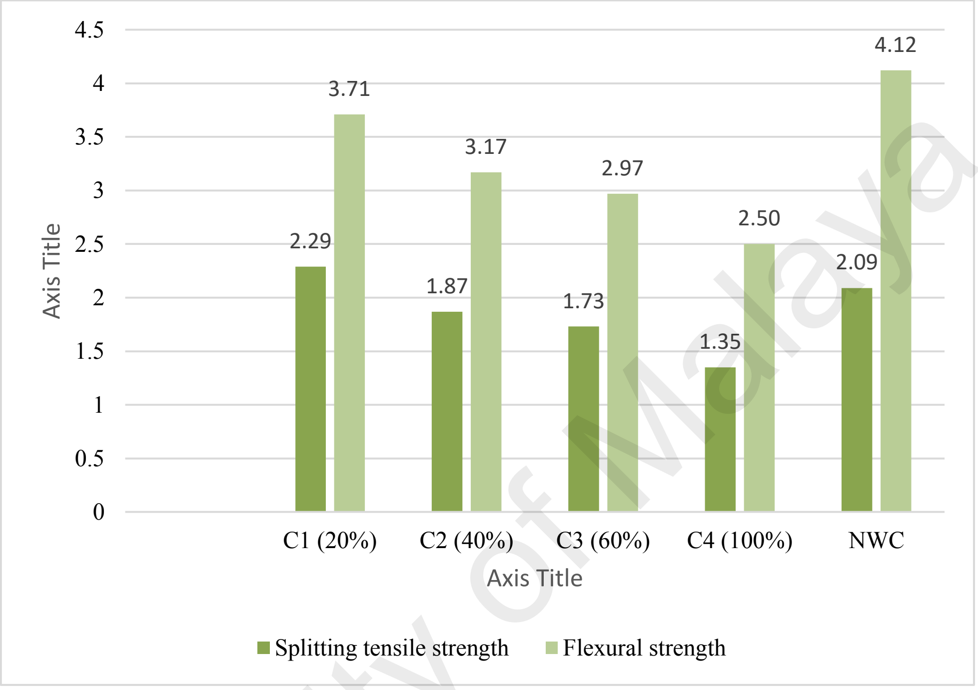

Figure 4.17 Flexural Tensile strength vs Splitting Tensile Strength

These results are compared with Honnakkalavar et al. (2018). After 28 days of curing, the maximum split tensile strength and flexural strength are obtained for the 40% CS replacement that are 2.77N/mm^2 and 4.1N/mm^2, greater than conventional mix results, which are 2.35N/mm^2 and 2.04N/mm^2 respectively.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The objective of the study was to explore the potential usage of abrasive blasting waste (ABW) from shipyard repair which is listed by Department of Environment Malaysia as scheduled waste SW104 as construction material namely bricks and concrete after treated by stabilization and solidification (S/S) method using Portland cement as a main binder.

This work has investigated the optimum design parameters of water to cement ratio (w/c), cement to ABW ratio (C/ABW) and the percentage of ABW replacement for sand as fine aggregates using the performance indicators of unconfined compressive strength of the monolith and leachability of the solidified waste. The binder and solidified ABW properties were also investigated, which include physical, chemical and microstructure through numerous means of methods.

Based on the conducted experiments and results, the main conclusions can be made from a series of S/S performance parameter tests. The finding of the research can be classified into three areas namely strengths, leachability and microstructure.

The following objectives were met in this research:

1. To characterize the abrasive blasting waste (ABW) in terms of its physical and chemical characteristics.

   The physical shape of ABW was colloidal, sharp and angular, which are very good for interlocking with the cement paste. By using ICP-OES, it was observed that the waste is chemically consists of ten heavy metal elements which are Arsenic (As), Barium (Ba), Cadmium (Cd), Chromium (Cr), Copper

(Cu), Nickel (Ni), Plumbum (Pb),Vanadium (V), and Zink (Zn). Out of these ten elements, two elements; Copper with concentration of 9932 mg/kg and Zink with concentration of 110467 mg/kg exceeded the allowable limit outlined by the Malaysia Department of Environment Regulation Guideline Limit (1989) which are 2500 mg/kg for Copper and 5000 mg/kg for Zink. Hence, the abrasive blasting waste needed to be treated to reduce the concentration of these two elements.

2. To determine the best design mix ratio in order to achieve acceptable compressive strength and leaching limit of solidified and stabilized cement-abrasive blasting waste paste.

   The strength development in the OPC is controlled by the w/c. The lowest w/c showed the optimum strength of the sample. The solidified OPC of w/c 0.3 performed better than higher range of w/c at the 28-day period. The solidified ABW was tested in w/c ratio of 0.3 to 0.5 range for an extended period of 56-day showed that the sample with w/c ratio 0.35 and C/ABW ratio of 1.5 gives the highest strength 53.37 N/mm^2. The strength was higher than the controlled OPC at the same w/c and curing period.

   The addition of spike metals in the solidified ABW has contributed to the increased in strength value. Consequently the spike metals being transformed into metal hydroxides that encapsulated the waste.

   All strength values were well above the US EPA stabilized material guidelines of 0.34 N/mm^2.

3. To establish the optimum compressive strength of cement-abrasive blasting waste to be applied as construction bricks.

After three main experiments namely compressive strength, water absorption and density tests were done, the solidified C/ABW brick is suitable to be categorized as Engineering Brick B (BS 3921:1985) as it satisfy the minimum requirement of compressive strength 50 MPa, water absorption less than 7% and density of more than 2100 kg/m^3.

C/ABW bricks was compared to two types of conventional commercial bricks namely clay bricks and sand-cement bricks in terms of compressive strength and density. The results has shown that the compressive strength of 20% C/ABW bricks at 28th day is 87.26% and 87.5% stronger than these bricks respectively.

4. To evaluate feasibility of using abrasive blasting waste as fine aggregates in concrete.

Due to the high specific gravity of ABW, the workability of fresh ABW concrete increased with the increase in the percentage of ABW replacing sand. The result obtained from the density shows that the samples containing 60% ABW as sand replacement has the highest density of 2333.26 kg/mm^3 compared to the control sample which has 2283.47 kg/mm^3. This is due to the presence of ABW with higher specific gravity compared to the mine sand. However, the compressive strength of the ABW concrete was highest at 20% replacement for sand.

5.2 Research Contribution towards Engineering Development and Contribution to Society

Solidification/stabilization (S/S) is a process that involves the mixing of a waste with a binder to reduce the contaminant leachability by both physical and chemical means and to convert the hazardous waste into an environmentally acceptable waste form for land disposal or construction use. S/S is a key treatment technology for the management of industrial hazardous wastes. According to the US Environment Protection Agency (USEPA), this treatment is known as Best Demonstrated Available Technology (BDAT).

S/S is also an increasingly popular technology for industrial property redevelopment and continues as a cornerstone treatment technology for the management of radioactive waste, hazardous waste, and site remediation. This application has potential in business plan and impacts on economic, environmental and socio-cultural. The treatment protects human health and the environment by immobilizing contaminants within the treated material. Immobilization within the treated material prevents migration of the contaminants to human, animal and plant receptors.

The application of this treatment including the area of business will be collecting, treating and marketing of metal waste from any industries that produces metal waste. S/S treatment process will create a treated product and will meet two critical needs:

a. It will help meet the growing demand for high strength concrete and concrete need for maintenance.
b. It will give consumers feasibilities and cost alternative rather than dumping or landfilling the waste.

The production of bricks from waste material will be targeted toward construction companies, landscapers, architectures, government agencies and other civil engineering company. Besides that, they can use the product of S/S treatment as high strength material for construction, concrete pavement, admixtures used in concrete and embankment materials. All of these potential customers will benefit from the improved S/S product.

In view of the environmental impacts, the solidification/stabilization treatment will result in resource and energy conservation, waste minimization, and extension of landfill capacity.

For socio-cultural impact, S/S treatment application may help in minimization of workers and human health impact by immobilizing contaminants within the treated material. And for the economy, the application has the benefit of eliminating disposal cost and lowering the cost of construction materials by replacement of the waste in cement.

5.3 Recommendation for Future Studies

1. Further research is recommended to understand the chemical properties and reaction which occur between the ABW and the cement when used as a mine sand replacement, as this will help understand the influence of ABW on cement and this will further enhance the knowledge.

2. At 60% ABW replacement of fine sand the workability is very high which may lead to segregation, it is recommended that the w/c should be change or revised for future researches.

3. The effects of ABW on the durability performance of HSC regarding freezing and thawing, corrosion, alkali-aggregate reaction, acid attack, and carbonation should be investigated.

4. The effect of elevated temperature on ABW concrete should be investigated for future research.

5. Predicting model shall be developed to determine the strength of other mixture proportion to wide range its applicability.

REFERENCES

Abdul Majid, Z., Mahmud, H. and Shaaban, M.G. (2001). Physical Characteristics and Leachability of Cement Solidified Waste. In: Din, K., Adnan, M.A. and Mohamad Nor, M.R. (Eds.). Current Trends in Concrete Engineering and Technology, *Proceedings of the Seventh International Conference on the Concrete Engineering and Technology*, 5-7 June 2001, Universiti Teknologi MARA. 242-257.

ACI SP-87 (1987). High-Strength Concrete. American Concrete Institute, Detroit.

Acosta, A., Iglasias, I., Aineto, M., Romero, R. and Rincon, J.M.A (2002). Utilization of IGCC slag and clay sterilse in soft mud brick (by pressing) for using in building bricks manufacturing. *Journal of Waste Management*, 22: 887-889.

Afiniwala, S., Patel, I., & Patel, N. (2013). Effect of High Volume Fly Ash on Rheological Properties of Self Compacting Concrete. *International Journal of Emerging Technology and advanced Engineering*, 3(7).

Akihiko Y, Takashi Y. (1996). Study of utilization of copper slag as fine aggregate for concrete. *Ashikaya Kogyo Daigaku Kenkyu Shuroku*, 23, 79-85.

Akhter, H., Cartledge, F.K., Roy, A., and Tittlebaum, M.E. (1997). Solidification/ Stabilization of arsenic salts: Effects of long cure times. *Journal of Hazardous Material*s, 52, 247-264.

Al-Jabri, K.S., Al-Saidy, A.H., and Taha, R. (2011) Effect of copper slag as a fine aggregate on the properties of cement mortars and concrete. *Construction and Building Material,* 25(2), 933-938.

Alnuaimi, A.S. (2012). Effects of copper slag as a replacement for fine aggregate on the behavior and ultimate strength of reinforced concrete slender columns. *Journal of Engineering Research*, 9(2), 90-102.

ANSI (2003). Measurement of the leachability of solidified low-level radioactive wastes by a short term method. American Nuclear Society, La Grange Park, IL.

Arniella, E., and Blythe, L., (1990). Solidifying traps hazardous wastes. *Chemical Engineering*, February, 92-102.

ASTM C127 (2004). Standard Method of Test for Specific Gravity and Water Absorption of Coarse Aggregate. American Society for Testing and Materials International.

ASTM C128-15 (2004). Standard Test Method for Relative Density (Specific Gravity) and Absorption of Fine Aggregate. American Society for Testing and Materials International.

ASTM C 109 (2005). Test Method for Compressive Strength of Hydraulic Cement Mortars. American Society for Testing and Materials International.

ASTM D5233 - 92 (2017). Standard Test Method for Single Batch Extraction Method for Wastes. American Society for Testing and Materials International.

Ayano Toshiki, Kuramoto Osamu, Sakata Kenji (2000). Concrete with copper slag fine aggregate. *Society of Materials Science*, 10(49), 1097-1102.

Barna, R., Sanchez, F., Moszkowicz, P. and Mehu, J. (1997). Leaching behavior of pollutants in stabilized/solidified wastes. *Journal of Hazardous Materials,* 52, 287-310.

Barth, E.F (1990). An overview of history, presents status and future direction of the solidification technologies for hazardous waste treatment. *Journal of Hazardous Materials,* 24, 103-109.

Batchelor, B. (1990). Leach models: Theory and applications. *Journal of Hazardous Materials*, 24, 255-266.

Bentz, D.P., Garboczi, E.J., Haecker, C.J, and Jensen, O.M. (1999). Effects of cement particle size distribution on performance properties of Portland cement-based materials. *Cement and Concrete Research*, 29, 1663-1671.

Bhatty, J.I. and West, P.B. (1996). Stabilization of Heavy Metals in Portland Cement Matrix: Effects on Paste Properties. *STP1240 Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes: 3rd volume.* American Society for Testing and Materials. 147 - 162.

Bijen, J. and Pletersen, H. (1994). Mineral admixtures: Reactions, microstructures and macro-properties, In: Grutzeck M.W. and Sarkar, S.L. (Eds.), Advances in Cement and Concrete, *Proceeding and Engineering Foundation Conference,* New Hampshire, Durham, 24-59 July, American Chemical Society of Civil Engineers, 292-328.

Bipra, G., Jana, R.K and Premchand (2003). Characteristics and utilisation of copper slag – a review. *Resources, Conservation and Recycling*, 39(2003) 299-313.

Birchall, J.D., Howard, A.J. and Bailey, J.E (1978). The hydration of Portland cement. *Proceedings Royal Society of London*. A360, 445-453.

Bishop, P.L. (1988). Leaching of inorganic hazardous constituents from stabilized/solidified hazardous waste. *Hazardous Waste and Hazardous Materials*, 5 (2), 129-143.

Boardman, D.I. (1999). Lime stabilization: Clay-metal-lime-interactions. PH.D. thesis, Loughborough University, United Kingdom.

Bonen. D. and Sarkar, S.L. (1994). The present state-of-the-art of immobilization of hazardous heavy metals in cement-based materials, In: Grutzeck, M.W. and Sarkar, S.L (Eds.), Advances In Cement and Concrete, *Proceedings of an Engineering Foundation Conference,* New Hampshire, Durham, 24-29 July, American Chemical Society of Civil Engineers, 481-498.

Bonen, D. and Sarkar, S.L. (1995). The effects of simulated environmental attack on immobilization of heavy metals doped in cement-based materials. *Journal of Hazardous Materials,* 40, 321-335.

Boyle W.C., Ham, R.K., Pastene, J. and Stanforth, R. (1983). Leach testing of foundry process wastes, In: R.A. Conwayand W.P. Gulledge, (Eds.), *Hazardous and industrial Solid Wastes Testing: Second Symposium,* ASTM STP805, 67-88.

Boss, C.B. and Fredeen, K.J. (1989). Concepts, Instrumentations and Techniques in inductively Coupled Plasma Atomic Emission Spectrometry: Perkin Elmer, 2-2.

Bricka, R.M. and Jones, L.W. (1992). An evaluation of factors affecting the stabilization/solidification of heavy metal sludge. *EPA Project Summary*. EPA/600/S-92/023 (May).

Brindha, D., Baskaran, T. and Nagan, S. (2010). Assessment of Corrosion and Durability Characteristics of Copper Slag Admixed Concrete. *International Journal of Civil and Structural Engineering,* 1(2), 194-208.

Brindha, D. and Nagan, S. (2011). Durability studies on copper slag admixed concrete. *Asian Journal of Civil Engineering (Building and Housing),* 12(5), 563-578.

BS EN 197-1 (2011). Cement. Composition, specifications and conformity criteria for common cements. British Standards Institution.

BS EN 12350-2 (2009).Testing Fresh Concrete. British Standards Institution.

BS EN 12390-3 (2009).Testing hardened concrete. Compressive strength of test specimen. British Standards Institution.

BS EN 12390-5 (2009). Testing hardened concrete. Flexural strength of test specimens. British Standards Institution.

BS EN 12390-6 (2009). Testing hardened concrete. Tensile splitting strength of test specimens. British Standards Institution.

BS EN 12390-7 (2009). Testing hardened concrete. Density of hardened concrete. British Standards Institution.

BS EN 1097-6:2013. Tests for mechanical and physical properties of aggregates. Determination of particle density and water absorption. British Standards Institution.

BS 6073-2:2008: Precast concrete masonry units. Guide for specifying precast concrete masonry units. British Standards Institution.

BS 3921 (1985). British Standard Specification for Clay Bricks. British Standards Institution

BS EN 771-3 (2011). Specification for masonry units: Aggregate concrete masonry units (dense and lightweight aggregates). British Standards Institution.

BS EN 933-1:2012. Tests for geometrical properties of aggregates. Determination of particle size distribution. Sieving method. British Standards Institution.

BS EN 196-3 (2016). Methods of testing cement. Determination of setting times and soundness. British Standards Institution.

Cassell, E.A., and Walker, T.W. (1970). Solidification of sludge with Portland cement. *Journal of Sanitary Engineering Division, Proceeding of the American Society of Civil Engineers,* February, 15-26.

Chan, W.W.J. and C.M.L (2000). Durability of concrete with high cement replacement. *Cement and Concrete Research*, 30, 865 – 879.

Chen Q.Y., Tyrer M., Hills C.D., Yang X.M., and Carey P. (2009). Immobilisation of Heavy Metal in Cement-Based Solidification/Stabilisation: A review. *Waste Management,* 29, 390-403.

Cheng-yi, Huang and Feldman, R.F. (1985). Hydration reaction of Portland cement- silica fume blends. *Cement and Concrete Research*, 15, 585 – 592.

Cheng, K.Y. and Bishop, P.L. (1992). Developing a kinetic leaching models for solidified/stabilized hazardous wastes. *Journal of Hazardous Materials*, 24, 213 – 224.

Cheng, K.Y. (1991). Controlling mechanism of metals released from cement-based waste form in acetic acidic solution. Ph. D. Thesis, University of Cincinnati, U.S.A.

Cheng, K.Y., Bishop, P. and Isenbugh, J. (1992). Leaching boundary in cement-based waste forms. *Journal of Hazardous Materials*, 30, 285 – 295.

Cheeseman, C.R., Sollars, J., and Perry, R. (1994). Mechanism of metal containment resulting from solidification of a commercially produced stabilized waste. In: Gilliam, T.M. and Wiles, C.C. (Eds.), *Stabilization and Solidification of Hazardous, Radioactive and Mixed Wastes: 3rd Volume ASTM STP 1240* (1996), American Society for Testing and Materials, Philadelphia.

Cheeseman, C.R., Butcher, E. J., Sollars, C.J, and Perry, R. (1993). Heavy metal leaching from hydroxide, sulphide and silicate stabilized/solidified wastes. *Waste Management*, 13(8), 545 – 552.

Chiu, S.W., Ho K.M., Chan, S.S., So, O.M., and Lai, K.H. (2006). Characterization of contamination in and toxicities of a shipyard area in Hong Kong. *Environmental Pollution,* 142, 512–520.

Choon-Kuen Park (2000). Hydration and solidification of hazardous waste containing heavy metals using modified cementitious materials. *Cement and Concrete Research,* 30, 429-435.

Cocke, D.L. (1990). The biding chemistry and leaching mechanism of hazardous substances in cementitious solidification/stabilization systems. *Journal of Hazardous Materials,* 24, 231-253.

Cocke, D.L. and Mollah, M.Y.A. (1992). The chemistry and leaching mechanisms of hazardous substances in cementitious solidification/stabilization systems. In: Spence, R.D (Ed.) *Chemistry and Microstructure of Solidified Waste Forms,* Lewis Publishers, Ann Arbor, 187-237.

Conner, J.R., Li, A. and Cotton S. (1990a). Stabilization of hazardous waste landfill leachate treatment residue. *Journal of Hazardous Materials,* 24, 111 – 121.

Conner, J.R. (1990b) Chemical Fixation and Solidification of Hazardous Waste. Van Nostrand, Reinhold, New York.

Conner, J.R (1993). Chemistry of cementitious solidified/stabilized waste forms. In: Spence, R.D (Ed.) Chemistry and Microstructure of Solidified Waste Forms, Lewis Publisher, Ann Arbor, 41 – 82.

Conner, J.R. and Hoeffner, S.L. (1998). The History of Stabilization/Solidification Technology. Critical Reviews in *Environmental Science and Technology*, 28 (4).

Cook, D.J. (1986). Natural pozzolanas. In: Swamy, R.N. (Ed.) Concrete Technology and Design: *Cement Replacement Materials*, Vol.3, London: Surrey University Press, 171 – 196.

Cote, P.L and Hamilton, D.P. (1983). Leachability comparison of four hazardous waste solidification processes. *Proceeding of 38th Industrial Waste Conference,* Purdure University, 221 – 231.

Cote, P.L. AMD Constable, T.W. (1983). Development of comparison of four hazardous waste leachability. In: R.A. Conway and W.P. Gulledge, (Eds.), *Hazardous Industrial Solid Waste Testing: 2nd Symposium, ASTM STP 805,* 53 – 66.

Cote, P.L (1986). Contaminant Leaching from Cement-based Waste Forms under Acidic Conditions, Ph. D. Thesis: McMaster University, Ontario, Canada.

Cote, P.L. and Bridle, T.R. (1987). Long-term leaching scenarios for cement-based waste forms. *Wastewater Management Research*, 5, 55 – 66.

Cote, P.L and Isabel, D. (1984). Application of a dynamic leaching test to solidify hazardous wastes. In: L.P. Jackson, A.R. Rohlik and R.A. Conways, (Eds.), *Hazardous Industrial Solid Wastes Testing: 3rd Symposium, ASTM STP 851*, 48-60.

Cullinane, Jr. M.j., Jones, L.W., Malone, P.G. and Houthoofd, J.M. (1986). Handbook for stabilization/solidification of hazardous wastes, U.S. EPA, EPA/540/2-86/001, (June), Hazardous Waste Eng. Res. Lab., Off. Of R&D, U.S EPA, Cincinnati, Ohio 04268.

Dames and Moore (1987). Toxic and hazardous waste study. Draft final report Feasibility study on treatment and disposal of toxic and hazardous waste in Malaysia. Submitted to Department of Environment, Malaysia, 7th December.

DOE Department of Environment Malaysia (1989). First Schedule of the Environmental Quality (Scheduled Wastes) Regulations, Malaysia.

DOE Department of Environment Malaysia (2005). Environmental Quality (Scheduled Wastes) Regulations 2005.

DOE Department of Environment Malaysia (2015). Malaysia Environmental Quality Report, 2015.

Department of Environment and Energy, Australia (2018). Hazardous Waste (Regulation of Exports and Imports) Act 1989.

Double, D.D. and Hellawell, A. (1977). The Solidification of Cement. *Scientific American*, 237(1), 82-90.

Douglas, E. and Zerbino, R. (1986). Characterization of granulated and pelletized blast furnace slag, *Cement and Concrete Research,* 16, 163-197.

Gambhir, M.L. (2005). Concrete technology. Third edition Tata McGraw-Hill Publishing Company Limited. New Delhi.

Geetha, S. and Madhavan, S. (2017). High Performance Concrete with Copper slag for Marine Environment. *Materials Today: Proceedings,* 4(2 Part A), 3525-3533.

Glasser, F.P. (1993). Chemistry of Cement solidified waste forms. In Spence, R.D (Ed.), Chemistry and Microstructure of Solidified Waste Forms, Lewis Publishers, Ann Arbor, 1 – 40.

Glasser, F.P. (1994). Environmental uses of cement in waste conditioning. In: Grutzeck, M.W. and Sarkar, S.L. (Eds), Advances in Cement and Concrete, *Proceedings of an Engineering Foundation Conference,* New Hampshire, Durham, 24 – 29 July, American Chemical Society of Civil Engineers, 499-507.

Glasser, F.P. (1997). Fundamental aspects of cement solidification and stabilization. *Journal of Hazardous Materials,* 52, 151-170.

Gorai B., Jana R. K., and Premchand, (2005). Characteristics and utilization of copper slag—a review. *Resour Conserv Recy*, 39, 299-313.

Goto, S. and Roy, D.M. (1981). The effect of w/c ratio and curing temperature on the permeability of hardened cement paste. *Cement Research*, 11, 575-579.

Gress, D.L. and EL-Korchi, T. (1993). Microstructural characterization of cement-solidified heavy metal wastes. In Spence, R.D (Ed.), Chemistry & Microstructure of Solidified Waste Forms, Lewis Publishers, Ann Arbor, 169-185.

Grube Jr., W.E. (1990). SITE program update. Evaluation of waste stabilized by the Solidtech SITE Technology. *Journal of Air & Waste Management Association*, 40(3), 310-316.

Honnakkalavar, A.H, Asif, M., Kallaganad, S.F., Vinay R, Ganesh S. R. and Shivakumar B. (2018). Experimental Study on concrete using Copper Slag as Replacement Material of Fine Aggregate. *International Research Journal of Engineering and Technology*, 5(5), 928-930.

Hills, C.D., Sollars, C.J. and Perry, R. (1992). Early heat of hydration during the solidification of metal planting sludge. *Cement and Concrete Research,* 23, 196-212.

Hills, C.D., Sollars, C.J. and Perry, R. (1993). Ordinary Portland cement based solidification of toxic wastes: The role of OPC reviewed. Cement-solidified hazardous waste forms. *Journal of Hazardous Materials,* 22, 822 - 832.

Hills, C.D. and Pollard, S.J.T. (1997). The influence of interference effects on the mechanical, microstructural and fixation characteristics of cement-solidified hazardous waste forms. *Journal of Hazardous Materials*, 52(2-3), 171-191.

Holmes, T.T. (1990). Comparison of contaminant leachability to quantity of binder material. *Journal of Hazardous Materials*, 24(133), 227-232.

Holmes, T.T., Kosson, D.S and Wiles, C.C. (1991). A comparison of five solidification/stabilization processes for treatment of municipal waste combustion residue – Physical testing. In: Gaumans, J.J.J.M, van der Sloot, H.A., Aalbers, Th. G., (Eds.), Waste Materials in Construction, Elsevier Science Publishers, Amsterdam, 107-118.

Jones, L.W. (1990). Interference mechanisms in waste stabilization/solidification processes, U.S. Environmental Protection Agency EPA/600/S2-89/067, January.

Josephson, J. (1982). Immobilization and leachability of hazardous wastes. *Environment Science and Technology,* 16, 219A-223A.

Kanagalakshmi, A. S. Prawinkiruthik, T., Settu, R., Sankar, J. and Vishnu, K. (2015). Experimental Investigation using Flyash, Copper Slag, Gypsum, Marble Dust as Smart Building Material in Brick Manufacturing. *International Journal of Mechanical, Civil, Automobile and Structural Engineering*, 1(1), 17-20.

Khanzadi, M., and Behnood, A. (2009). Mechanical properties of high strength concrete incorporating copper slag as coarse aggregate. *Construction and Building Material.* 23, 2183-2188.

LaGrega, M.D., Evans, J.C., Acuna, C.O., Zarlinski, S.J. and Hall, D.S. (1989). Stabilization of acidic refinery sludges. *Journal of Hazardous Materials*, 24, 169-187.

LaGrega M.D, Buckingham, P.L and Evans, J.C. (2010). Hazardous Waste Management: Second Edition. Waveland Press.

Lange, L.C., Hills, C.D. and Poole, A.D. (1997). Effect of carbonation of the properties of blended and non-blended cement solidified waste forms. *Journal of Hazardous Materials,* 52, 193-212.

Lea, F.M. (1970). The chemistry of cement and concrete, 3rd Ed., Edward Arnold Ltd., London.

Lim, T.T and J. Chu (2006). Assessment of the use of spent copper slag for land reclamation. *Waste Management & Research*, 24. 67-73.

Macias, A., Kindness, A. and Glasser, F.P. (1997). Impact of carbon dioxide on the immobilization potential of cemented wastes: Chromium. *Cement and Concrete Research*, 27(2), 215-225.

Macphee, D.E. and Glasser, F.P. (1993). Immobilization science of cement systems. *Materials Research Society Bulletin*, XVIII, No. 3. 66-71.

Mahendran, K., Nivetha M.B. and Kaleeswari P. (2017). Experimental Study on Low Cost Bricks Using Copper Slag And Rice Husk Ash. *SSRG International Journal of Civil Engineering.* Special Issue. 554-559.

Malaysian Association of Ship Owners (2011) Retrieved from the official website on 7 July 2012. http://www.masa.org.my/

Malliou O. (2006). Properties of Stabilized/Solidified Admixtures of Cement and Sewage Sludge. *Cement & Concrete Composites.* 29(1), 55-61.

Malone, P.G. and Larson, R.J. (1983). Scientific basis of hazardous waste immobilization. In: R.A. Conway and W.P. Gulledge, (Eds.). *Hazardous and Industrial Solid Waste Testing Second Symposium,* ASTM STP 805, 168-177.

Mannan, M.A, Basri, H.B., Zain, M.F.M, Islam, M.N. (2002). Effect of curing conditions on the properties of OPS concrete. *Building and Environment.* 37, 1167-1171.

Mehu, J., Perrodin, Y., Sarrazin, B. and Veron, J. (1991). French approach towards the evaluation of monolithic and solidified waste: Development of a new leaching procedure. In: Gaumans, J.J.J.M., van der Sloot, H.A. Aalbert, Th. G., (Eds.) *Waste Materials in Construction*, Elsevier Science Publishers B.V., Amsterdam, 293-300.

Mehta, P.K. (1998). Role of fly ash in sustainable development. *Concrete, Fly ash, and Environment Proceedings.* EHDD Architecture and Pacific Energy Center. http://www/buildinggreen.com/features/flyash/mehta.cfm. Retrieved on 9/7/11.

Mehta, P.K. (1987). Natural Pozzolans. In: Malhotra, V.M. (Ed.) *Supplementary Cementing Materials for Concrete,* Canada: Minister of Supple and Services Canada, 3 -31.

Mehta, P.K. (1981). Studies on blended Portland cements containing Santorin earth. *Cement and Concrete Research,* 11, 507 – 518.

Mobasher, B., Devaguptapu, R., Arino A.M. (1996). Effect of copper slag on the hydration of blended cemetitious mixtures. In: Chong K, editor. *Proceedings of the ASCE Materials Engineering Conference, Materials for the New Millennium.* 1677-1686.

Montgomery, D.M., Sollars, C.J., and Perry, R. (1988). Cement-based solidification for safe disposal of heavy metal contaminated sewage sludge. *Waste Management & Research*, 6, 217-226.

Montgomery, D.M., Sollars, C.J., Perry, R., Tarling, S.E., Barnes, P., and Henderson, E. (1991). Treatment of organic-contaminated industrial wastes using cement-based stabilization/solidification – I. Microstructural analysis of cement-organic interactions. *Waste Management & Research*, 9, 103-111.

Moszkowicz, P., Sanchez, F., Barna, R. and Mehu, J. (1998). Pollutants leaching behavior from solidified wastes: A selection of adapted various models. Talanta, 46, 375-383.

Moura, W.A, Goncalves, J. P., and LeiteLima, M. B. (2007). Copper slag waste as a supplementary material to concrete. *Journal of Materials Science*, 42(7), 2226-2230.

MS: 522: Part 1: 2003 Portland Cement (ordinary and rapid-hardening). Part 1 Specification. Malaysia Standards.

Myers, J.J., Carrasquillo, R.L. (1999). The Production and Quality Control of High Performance Concrete in Texas Bridge Structures. Center for Transportation Research, Preliminary Report Number 580-589-1, Submitted November 1999.

Nazer, A.S., Pavez, O., and Rojas, F. (2012). Use of copper slag in cement mortar. *Metallurgy and Materials*, 65(1).

Nazer, A., Paya, J., Borracherro, M.V, and Monzo, J (2016). Use of ancient copper slags in Portland cement and alkali activated cement matrices. *Journal of Environmental Management*. 167, 115-123.

Neville, A.M. (1995). Properties of concrete. 4th. Edition, Addison Wesley Longman Ltd., England.

Neville, A.M. and Brooks, J.J. (1987). Concrete technology. ELBS/Longmans, Singapore.

Nontananandh, S. (1990). Industrial Waste Utilization as Construction Materials by Chemical Stabilization, Dr. Eng. Thesis, University of Kyoto, Japan.

Ortego, J.D. (1990). Spectroscopic and leaching studies of solidified toxic metals. *Journal of Hazardous Materials,* 24, 137-144.

Palmark, M. (1985). Types of chemical wastes. In: Muller, K.R. et al. (Eds.), *Chemical Waste Handling and Treatment,* Springler-Verlag, Berlin, 31-67.

Pan, Z., Zhang, J. and Liu, W. (2015). Solidification /stabilization of zinc-lead tailings by alkali activated slag cement. Journal of Wuhan University of Technology - *Mater. Sci. Ed.*, 30(1), 105-108.

Park, C.K. (2000). Hydration and solidification of hazardous wastes containing heavy metals using modified cementitious materials. *Cement and Concrete Research*, 30, 429-435.

Park, J.Y. and Batchelor, B (1999). Prediction of chemical specification in stabilized/solidified wastes using a general chemical equilibrium model: Part 1. Chemical representation of cementitious binders. *Cement and Concrete Research, 29, 361-368.*

Pavez, O., Rojas, F., Palacios, J. and Nazer, A. (2002). Pozzolanic activity of copper slag. *Proceedings of the VI National Conference on Clean Technologies for the Mining Industry,* Chile.

Pollard S.J.T., Montgomery, D.M., Sollars, C.J. and Perry, R. (1991). Organic Compounds in the cement-based stabilization/solidification of hazardous mixed wastes-Mechanistic and process consideration. *Journal of Hazardous Materials*, 28, 313-327.

Poon, C.S. (1985). Cement-based stabilization and solidification techniques for hazardous waste disposal. Ph. D Thesis, Imperial College of Science and Technology, University of London, London, England.

Poon, C.S., Clark, A.I., Peters, C.J. and Perry, R. (1985). Mechanism of metal fixation and leaching by cement based fixation processes. *Waste Management & Research*, 3, 127-142.

Poon, C.S., Peters, Perry, R. (1985). Mechanism of metal stabilization by cement based fixation process. *The Science of Total Environment,* 41, 55 – 71.

Poon, C.S., Clark, A.I., Perry, Baker, A.P. and Barnes, P. (1986). Permeability study on the cement based solidification process for the disposal of hazardous wastes. *Cement and Concrete Research*, 16, 161-172.

Poon, C.S. (1989). A critical review of the evaluation procedures for stabilization/solidification processes. In: Cote, P.L and Gilliam, T.M. (Eds.) *Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Wastes*, ASTM STP 1033, 114-124.

Pojasek, R.B. (1978). Stabilization, solidification of hazardous wastes. *Environmental Science & Technology,* 12(4), April, 383-386.

Ramachandran, V. (1976). Hydration of cement – Role of triethanolamine. *Cement and Concrete Research*, 6, 623-631.

Rashid, M.A and Mansur, M.A. (2009). Considerations in producing high strength concrete. *Journal of Civil Engineering* (IEB), 37(1), 53-63.

Raut, S.P., Ralegaonkar, R.V. and Mandavgane, S.A. (2011). Development of sustainable construction material using industrial and agricultural solid waste: A review of waste-create bricks. *Journal of Construction and Building Material*, 25: 4037-4043.

Rechenberg, W., Sprung, S., Sylla, H.M (1991). A test method for the determination of the leachability of the trace elements from wastes bound with cement. In: Gaumans, J.J.J.M., van der Sloot, H.A., Alberts, Th. G., (Eds.), *Waste Materials in Construction,* Elsevier Science Publisher B.V., Amsterdam, 301-309.

Reddy, K.B.P., Tanuja, K. and N.Vasu Deva Naidu, N.V.D (2016). Use of Copper Slag in Concrete and Cement Mortar as Replacement of Sand. *International Research Journal of Engineering and Technology,* 03(9), 254-260.

Roy, D.M. ad Scheetz, B.E. (1993). The chemistry of cementitious systems for waste management: The Penn state experience. In Spence, R.D (Ed.). *Chemistry and Microstructure of Solidified Waste Forms.* Lewis Publishers, Ann Arbor, 83-101.

Salleh, S. and Dayanand, U.D. (2016). Effect of Using Copper Slag as Sand Replacement in Mortar. *NZAAR International Event Series on Natural and Built Environment, Cities, Sustainability and Advanced Engineering.* 26 June 2016. Putrajaya, Malaysia.

Sharma R. and Khan R.A (2017). Sustainable use of copper slag in self compacting concrete containing supplementary cementitious materials. *Journal of Cleaner Production,* 151, 179-192.

Shi C., Christian M., and Behnood A. (2008). Utilization of copper slag in cement and concrete. *Resources, Conservation and Recycling*, 52(10), 1115-1120.

Silva A.R.M. (2007). Small Hazardous Waste Generators in Developing Countries: Use of Stabilization/Solidification Process as an Economic Tool for Metal Wastewater Treatment and Appropriate Sludge Disposal; *Journal of Hazardous Materials.* 147(3), 986-990.

Sollars, C.J. and Perry, R. (1989). Cement-based stabilization of wastes: Practical and theoretical considerations. *Journal Institution of Water Engineering Management,* 3, (April), 125-134.

Stegemenn, J.A. and Cote, P.L. (1990). Summary of an investigation of test methods for solidification waste evaluation. *Waste Management*, 10. 41-52.

Tam, C.T. (2003). Constituents and properties of concrete. *Civil Engineering Handbook*, CRC Press LLC.

Tamil Selvi, P., Lakshmi Narayani, P., Ramya, G. (2014). Experimental Study on Concrete Using Copper Slag as Replacement Material of Fine Aggregate. *J Civil Environ Eng*, 4(156).

Tashiro, C., Takahashi, H., Kanaya, M., Hirakida, I. and Yoshida, R. (1977). Hardening property of cement mortar adding heavy metal compound and solubility of the heavy metal from hardened mortar. *Cement and Concrete Research,* 7, 283-290.

Taylor, H.F.W. (1990). Cement Chemistry, Academic Press Inc., New York.

Teo DCL, Mannan MA, Kurian VJ, Zakaria I (2006). Flexural Behaviour of Reinforced Lightweight OPS Concrete Beams. *9th International Conference on Concrete Engineering and Technology,* Malaysia, 244-252.

Third Industrial Master Plan (IMP3) (2006). Retrieved from official website on 7 July 2012. http://www.miti.gov.my/

Thompson, D.W., Malone, P.G. and Jones, L.W. (1979). Survey available stabilization technology. In: Pojasek, R.B. (Ed.). Toxic and Hazardous Waste Disposal (Vol. I: Process for stabilization/solidification). Ann Arbour Science Publishers, Inc., U.S.A.

Tittlebaum, M.E., Seals, R.K., Cartledge, F.K., and Engels, S. (1985). State-of-the-art on stabilization of hazardous organic wastes and sludges. In: Straub, C.P. (Ed.) Critical Reviews in Environmental Control, 15(2), CRC Press, Boca Rota, Florida, 179-21.

Tixier R, Arino-Moreno A, Mobasher B. (1996). Properties of cementitious mixture modified by copper slag. *Symposium: HH, Structure-Property Relationships in Hardened Cement Paste and Composites*. Tucson, Arizona, USA: Minerals Research and Recovery.

US EPA (1982a). Test methods for evaluating solid waste. Physical/Chemical methods. 2nd. Ed. SW-846. United States Environmental Protection Agency. Office of Solid Waste and Emergency Response, Washington.

US EPA (1982b). Guide to the Disposal of Chemically Stabilized and Solidified Waste. SW-872 (September). United State Environmental Protection Agency.

US EPA (1986). Handbook for Stabilization/Solidification of Hazardous Wastes. EPA/540/2-86/001 (June). United State Environmental Protection Agency.

US EPA (1989). Stabilization/Solidification of CERLA and RCRA Wastes. Physical Test, Chemical Testing Procedures Technology Screening and Field Activities. EPA/625/6-89/022 (May). United State Environmental Protection Agency.

US EPA (1990). Test Method 1311, Toxicity Characteristic Leaching Procedure; U.S. Environmental Protection Agency.

US EPA (1993). Solidification/ Stabilization and its application to waste materials. EPA/530/R-93/012. United States Environmental Protection Agency.

US EPA (2000). A Guide for Ship Scrappers - Tips for Regulatory Compliance. U.S. Environmental Protection Agency, Office of Enforcement and Compliance Assurance, Federal Facilities Enforcement Office. EPA 315-B-00-001.

US EPA (2005). Introduction to Hazardous Waste Identification; U.S. Environmental Protection Agency. EPA530-K-05-012.

Van der Sloot, H.A. (1986). Modelling chemical interactions at a waste/waste interface. *Environmental Technology Letters*, 10, 969-976.

Van der Sloot, H.A. (1991). Systematic leaching behavior of trace elements from construction materials and waste materials. In: Gaumans, J.J.J.M., van der Sloot, H.A., Aalberts, Th. G., (Eds.), *Waste Materials in Construction,* Elsevier Science Publishers B.,Amsterdam, 19-36.

Velumani, M., Sowmiya, G., Siva, K., Ram Kumar, S. and Shiva, M. (2016). An Experimental Study of Copper Slag and Discarded Tyre Materials for the Manufacturing of Concrete Brick. *International Journal for Scientific Research & Development*, 3(12), 1042-1044.

Vipulanandan, C. and Krishnan, S. (1990). Solidification/Stabilization of organic phenolic waste with cementitious and polymeric materials. *Journal of Hazardous Materials,* 24, 123-136.

Weitzman, L. (1990). Factors for selecting appropriate solidification/stabilization methods. *Journal of Hazardous Materials*, 24, 157-168.

Wentz, C.A. (1989). *Hazardous Waste Management*. McGraw Hill, New York.

Wiegrink K, Marikunte S, Shah S.P. (1996). Shrinkage cracking of high strength concrete. *ACI Mat. J.*, 93(5): 409-415.

Wienerberger (2018). https://wienerberger.co.uk/about-us/engineering-bricks. Retrieved on 3 September 2018.

Wilding, C.R., Walter, A. and Double, D.D. (1984). A classification of inorganic and organic admixtures by conduction calorimetry. *Cement and Concrete Research*, 14, 185-194.

Wiles, C.C. (1988). Evaluation of solidification/stabilization for treating hazardous wastes in the United States. In: R. Abbou (Ed.). *Hazardous wastes: Detection, control, treatment.* Elsevier Scientific Publication, Amsterdam.

Wilk, C.M. (2007). Solidification/Stabilization Treatment and Examples of Use at Port Facilities. Portland Cement Association.

LIST OF PUBLICATIONS AND PAPERS PRESENTED

Salmaliza Salleh, Md Ghazaly Shaaban, Hilmi B. Mahmud (2012). Compressive Strength of Cement-Based Solidification and Stabilisation of Metal Waste from Shipyard Repair. The 10th International PSU Engineering Conference, Thailand.

J. Kang, Md Ghazaly Shaaban, U.J.Alegaram and **Salmaliza Salleh** (2012). Compressive Strength Evaluation of Stabilized and Solidified Metal Waste from Shipyard. 11th International Conference on Concrete Engineering and Technology, Putrajaya.

Salmaliza Salleh, Md Ghazaly Shaaban, Hilmi B. Mahmud, J. Kang, and K.T. Looi (2013). Production of Bricks from Shipyard Repair and Maintenance Hazardous Waste. International Journal of Environmental Science and Development, Vol. 5, No. 1. p52-55.

Salmaliza Salleh, Md Ghazaly Shaaban, Hilmi B. Mahmud (2013). Production of Alternative Bricks from Shipyard Repair and Maintenance Hazardous Waste, International Conference on Environmental Prevention and Pollution, Melaka.

Salmaliza Salleh and Rishanthi.T (2014). Comparison of Engineering Properties between Pure Copper Slag Brick and Spent Copper Slag Brick. International Journal of Mechanical and Production Engineering (IJMPE), pp. 31-35, Volume-3,Issue-9.

Salmaliza Salleh, and Mohamad Khalife (2015). Evaluation on Compressive Strength of Spent Copper Slag Short Column Masonry. International Journal of Advances in Mechanical and Civil Engineering, ISSN: 2394-2827 Volume-2, Issue-4, Aug.-2015.

Salmaliza Salleh, Md Ghazaly Shaaban, Hilmi B. Mahmud, and Suresh Rao (2015). The Compressive Strength of Flemish Bond Wall by Exploiting Spent Copper Slag from Shipyard Waste. Applied Mechanics & Materials. Vol. 700, p407-412.

Salmaliza Salleh and Umanee Dasan Dayananda (2016). Effect of Using Copper Slag as a Sand Replacement in Mortar. International Conference on Civil Engineering, Advanced Structures and Construction Management (ICCEASCM 2016), Kuala Lumpur.

Rishanthi Tamil Selvan and **Salmaliza Salleh** (2016). Comparison of Properties between Pure & Spent Copper Slag Brick. LAP LAMBERT Academic Publishing. ISBN-10: 3659847526. ISBN-13: 978-3659847523