Treated Used Engine Oil as a Concrete Admixture

By

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CERTIFICATION OF APPROVAL

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TRONOH, PERAK

September 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(Koo Ting Choong)

ABSTRACT

Over the years, plenty of studies have proven that the used engine oil (UEO) can be used as a concrete admixture to improve workability and also the air content of the concrete, thus making UEO a potential green alternative to the traditional water reducers and air entrainment agents.

However, the UEO have a wide range of impurities, and some of the impurities are ionic compounds, such as acids, sulphates, phosphates, chlorides and heavy metal oxides which are traditionally harmful components towards the durability of concrete.

Purpose of this project is to treat the UEO using ionic liquid (IL), determine the effects of different types of UEO, as well as their constituent on concrete in terms of workability, compressive strength and porosity. A total of 5 UEO samples collected from different sources and 5 different ILs are tested for performance of phase separation first. ILs used in this project are: 2-hydroxy ethylammonium formate (HEF), bis(2-hydroxylethyl) methyl ammonium formate (BHEF), 2-hydroxyethyl ammonium acetate (HEA), 1-n-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]), and 1-butyl-3-methylimidazolium acetate ([bmim][Ac]). Samples of UEO are mixed with IL at 1:1 ratio for extraction, where mixture stirred at 500rpm for 30 minutes, and then left for settlement for 3 days. HEF is chosen to produce treated UEO (TUEO) due to overall better phase separation. Impurities removal rates by HEF are roughly estimated, where it is noted to be efficient at extracting SO_3, CaO, ZnO and MgO. Unfortunately, HEF causes an increase in acidity in two TUEO samples, which cause decreased concrete strength.

Slump tests showed little differences between UEO and TUEO slumps. High acidity in admixture (UEO and TUEO) has been found to greatly decrease the concrete strength, while admixtures that are not acidic maintain the concrete strength. Porosity of concrete with UEO and TUEO are found to be slightly higher than control mix.

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1. INTRODUCTION

In this chapter, background of the research on utilizing used engine oil (UEO) as a water reducer/super-plasticizer and air-entraining agent is briefly introduced. Problems and short-coming of UEO as a concrete admixture are discussed prior to the development the objective for this project. Last but not least, scopes of work of this project are also listed out.

1.1 Project Background

There is a current trend all over the world to investigate the utilization of processed and unprocessed industrial by-products and domestic wastes as raw materials in cement and concrete. Processed or unprocessed industrial by-products or wastes can be used as raw materials in cement manufacturing, as components of concrete binder, as aggregates, a portion of aggregate, or ingredients in manufactured aggregates. Some wastes can be used as chemical admixtures and additives, which can alter and enhance selected properties of fresh and hardened concrete [6].

One of the most abundantly produced wastes is used engine oil (UEO). It is estimated that less than 45% of the used-engine oil is being collected worldwide while the remaining 55% is thrown by the end user in the environment, which had caused serious pollution to the environment, especially to the water sources [8]. Oil films on top of water surface stops the photosynthesis of aquatic plants and preventing oxygen replenishment of the water, which ultimately leading to the death of the underwater life. In addition, used oil contains some toxic materials that can reach humans through the food chain. Health hazards range from mild symptoms to death.

Without doubt UEO is a waste which can be recycled or reuse. Most common recycling of UEO is using it as a crude lubricant for machineries. UEO can also be re-refined into new lube oil or fuel oil. However refining UEO would require well developed waste-oil collection system, as well as the technology in the refineries [1,8]. These would require well developed market and extensive capital investment to be realised, thus imposing financial and technological pressure especially on the less developed countries.

Meanwhile, it is reported that leakage of oil into the cement in older grinding units has led to a greater resistance to freezing and thawing in the concrete [1,2,3,4,5,7]. Accordingly, adding used engine oil to the fresh concrete mix could be similar to adding an air-entraining chemical admixture, thus enhancing some durability properties of concrete while serving as a technique of disposing the oil waste. Air entrainment is recommended principally to improve the freeze–thaw resistance of hardened concrete. As the water in moist concrete freezes, it produces osmotic and hydraulic pressures in the capillaries and pores of the cement paste and aggregate, which will cause cavities to dilate and rupture if the pressure exceeds the tensile strength of the cement paste. Entrained air also improves the workability of concrete, reduces segregation and bleeding in freshly mixed and placed concrete, and increases pump-ability of fresh concrete if introduced in low percentages up to 6% [1].

Since then, there have been researchers investigating effects of oil on concrete when used as a chemical admixture. Aware that there is a need to reduce such impact, plenty of researchers have turned their heads to the utilization of UEO for concrete applications. Studies carried out by Bilal et. al.(2003) [1] have shown adding 0.075, 0.15 and 0.30% UEO in concrete by weight of cement have improved slump (workability) and air emtrainment of the concrete, while maintaining the compressive strength. Other researchers have also confirm the benefits of UEO when used as a concrete admixture [2][3][4][5]. It is also noted that UEO can give superior performance which is comparable to super-plasticiser when used on different types of concrete, where it improves workability, flexural and compressive strength.

Given the cost, performance and environmental benefits, UEO certainly can be a 2-in-1 alternative to the traditional super-plasticizer and air-entraining agent.

1.2 Problem statement

Unfortunately, despite the fact that usage of UEO in concrete has yield positive results, UEO contain various impurities such as compounds of heavy metals, magnesium, phosphate, sulphate and chloride, which are commonly known as concrete damaging chemical components. Heavy metal salts have been found to affect the hydration of cement paste, phosphates can retard the hydration of cement minerals, Some UEOs are also found to be slightly acidic, with pH value between 6 to7 [1]. As main component of concrete exist in stable equilibrium in pore waters of high pH (12.5 to 13.5), contact with acidic ions of hydrogen ion, carbonates, sulphates and chlorides will have adverse effects on concrete [11,15,16].

Findings by Gamal et al [3] shows when UEO is used (0.15%, 0.30 and 0.60%), 28-day compressive strength, homogeneity and density of OPC concrete can be slightly degraded when compared to the control mix which has no UEO. Although the reason for this phenomenon is uncertain, the possible causes could be the increase of porosity in concrete due to the air entraining capabilities of UEO, as well as the slightly lower hydration degree of the calcium silicate hydrates (C-S-H) due to the existence of phosphates, sulphates and chlorides. Effects of these compounds on concrete will be further explained in the literature review.

In a research on structural performance of reinforced concrete beams containing used engine oil by a UTP phD students S.C.Chin [5], it is found that when new engine oil is used instead of used engine oil at the same dosage, ultimate load achieved by the beam is slightly higher. This has again hinted that the impurities in the UEO might have contributed to the weakening of the concrete

Currently there is also lacking of experimental findings regarding the effects of different types of UEO and its constituent on concrete. It is important to study these effects since there are many different types of engine oil in the market with varying chemical and physical properties. UEO of different type of base oil and additives package might have different physical properties such as viscosity index, and chemical properties which can affect its lubricating ability. Besides, even UEO from two different sources with the same type of base oil have different chemical impurities/constituent, as it might have gone through a very different internal combustion process, with used period, type of engine, type of fuel and environmental conditions as variables. Due to this large variety of UEO, it is certain that different UEO from different sources will give varying outcome to the concrete when it is used as an admixture.

1.3 Project objectives

The objectives of this project are:

1. To develope a treatment process for UEO, which extracts of impurities (phosphates, sulphates, and chlorides) using ionic liquids to produce a much benign UEO towards concrete.
2. To determine the effects of different UEO on fresh and hardened concrete properties.
3. To determine the effects of UEO constituents on fresh and hardened concrete properties.

1.4 Scope of Work

The scope of work for the project has been divided into three categories as below:

1.4.1 *Chemical analysis of UEO samples*

Studies of chemical composition of the UEO will be carried out twice in this project: before treatment and after treatment. Analysis of UEO before treatment will provide accurate information on the types and percentage of impurities. This will open the path towards selection of the type of ionic liquids and extraction procedures. Analysis of UEO after treatment will be necessary to find out the effectiveness of the treatment process – amount of residual impurities in the treated UEO.

1.4.2 *Treatment of UEO*

This process is to remove concrete damaging impurities through solvent extraction method by ionic liquid. Procedures of such treatment method will be determined later after selection of type of ionic liquid to be used.

1.4.3 *Concrete testing*

Two sets of concrete mixes with varying percentage UEO content will be made: Set 1 with untreated UEO and Set 2 with treated UEO. Fresh and hardened properties such as slump of fresh concrete, porosity, compressive strength will be studied and compared.

2. LITERATURE REVIEW

This chapter consist of literature from various journals which discuss: constituent of used engine oil, effect of water reducers/super-plasticizer on concrete, potential chemical deterioration of concrete by chemical compounds found in UEO, and the potential of using ionic liquid to extract impurities from UEO using liquid-liquid extraction method.

2.1 Constituent of Used Engine Oil

Other than hydrocarbon based oil, the used engine oil is contaminated by a number of impurities [17,18]. The impurities are from the additives of the engine oil, degradation process of the addictives during the combustion of the fuel, mechanical wear of the engine pistons, and external contaminants such as dirt and water. Commercial motor/engine oil is a combination of a heavy hydrocarbon base stock and an additive package [17,18]. This addictives often reach the amount of 10% of the oil. Addictive packages compose of detergent, dispersants, buffers, solvent, emergency lubricants, viscosity index improvers and corrosion inhibitors (antioxidant), which are varying chemicals. Typically, the addictives mainly consist of Ca based organic compounds. For instance, buffers of engine oil, which are typically consist of compounds of calcium, magnesium, or boron, are chemicals that neutralize the acids form in the engine due to oxidization from heat and pressure. During internal combustion, the addictives will be combusted and form ashes/salts such as CaO and MgO that will remain in the engine oil. Sulphuric acids are more common ones as residual sulphur or sulphates in the fuel or lubricant (engine oil) can be oxidized and become acids. Emergency lubricants consist of molybdenum disulfide. Given the chemical content of the additives of engine oil, it is easy to assume that most UEO consist of oxidized form of the aforementioned compounds. Chemical analysis of UEO from Beddu et al [2] has confirmed that sulphates exist in abundance (37% of UEO), while phosphates and chlorides are 8.95% and 15.9% respectively. Depending on the age/usage of UEO, phosphoric and sulphuric acids could exist in UEO if the buffers are all used up or expired. Besides the acidity, acid-base reaction from the buffers and acids will cause formation of suspended sulphate salts of magnesium, calcium and boron in UEO can also have adverse effects on concrete.

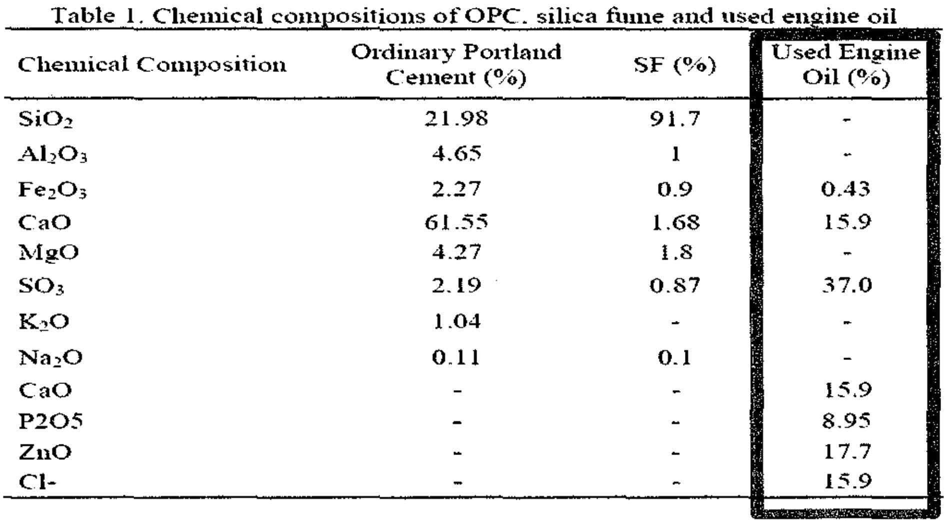


Table 1. Chemical compositions of OPC, silica fume and used engine oil

Chemical Composition	Ordinary Portland Cement (%)	SF (%)	Used Engine Oil (%)
SiO_2	21.98	91.7	-
Al_2O_3	4.65	1	-
Fe_2O_3	2.27	0.9	0.43
CaO	61.55	1.68	15.9
MgO	4.27	1.8	-
SO_3	2.19	0.87	37.0
K_2O	1.04	-	-
Na_2O	0.11	0.1	-
CaO	-	-	15.9
P2O5	-	-	8.95
ZnO	-	-	17.7
Cl-	-	-	15.9

Figure 1: UEO composition by Beddu et al.

2.2 Effects of water reducers/super-plasticizer on concrete

Most concrete produced today includes either chemical additions to the cement, chemical admixtures in the concrete, or both [10]. These chemicals alter a number of properties of cementitious systems, including hydration behaviour, thus affecting the properties of fresh concrete as well as the properties of hardened concrete. Today, admixtures commonly used in production concrete can contain set retarding or set accelerating chemicals, while most concrete made in developed countries also uses at least a cement dispersing agent, commonly called water reducing or plasticizing admixture. These water reducing admixtures that can exhibit a more powerful dispersing capability, without significantly impacting setting behavior, are called high-range water reducing admixture or superplasticizer.

Improved dispersion by these materials can improve workability or flowability of the concrete, as well as reducing the amount of agglomerated cement particles, which can improve homogeneity of the concrete. These agglomerates can lead to low w/c regions, which limits cement hydration in those areas, while allowing other regions to be higher than nominal w/c. Such agglomerates, formed during the initial mixing of Portland cement with water, result from relatively large Van der Waals forces of attraction, which operate at inter-particle distances in the range of 5 to 7 nm. Loosely entrapped quantities of water are associated with the agglomerated network of particles. WR/HRWR admixtures have the ability to overcome the Van der Waals attractive inter-particle forces by imparting a stronger repulsive force at the surface-liquid interface, freeing the entrapped water.. Thus water reducing admixtures can often lead to improvement in strength and permeability even at equal w/c.

While many of admixtures have the primary impact that can provide dispersing effect, inhibit corrosion of steel in concrete, adjust complex rheological behaviour, entrain air to impart resistance to freezing and thawing, they can also have secondary impact on the hydration kinetics of cement paste which retard or accelerate the hydration process. This is mainly due to their chemical composition, which might contain such hydration retarding impurities in order to meet economical constraints.

2.3 Chemical deterioration of concrete

Topics under this sub-chapter discuss the effects of each chemical compounds found in the UEO on concrete. Deterioration of concrete by chemical reaction can occur mainly in three forms: exchange reactions between aggressive fluid and components of hardened cement paste, and reaction involving formation of expansive products, and reaction involving hydrolysis and leaching of the components of hardened cement paste [11]. Form of deterioration will be dependent on the chemical compounds exposed to concrete, which normally attack concrete in solution phase.

2.3.1 Effects of magnesium salts on concrete.

Presence of magnesium ions in concrete can have deleterious effects [9, 11, 16]. Solutions containing magnesium salts of chloride, sulphate or bicarbonate can have exchange reactions with calcium hydroxide in hardened cement paste, which will form soluble salts of calcium. As magnesium salts are also sparingly soluble, formed magnesium salts might be leached away by pore waters of concrete, which will cause the concrete to weaken over the loss mass. Magnesium ions attack can extend to the calcium silicate hydrate (C-S-H), where C-S-H gradually loses calcium and partially replaced by magnesium ions. This new product of magnesium silicate hydrate has no cementitious or binding characteristics. $MgSO_4$ is particularly more destructive than other magnesium salts, as it can cause decalcification of calcium silicate hydrates and other cementitious minerals, as well as contributing to sulphate attack due to its SO_4^{2-} anion. Effects of sulphates will be discussed later.

2.3.2 Effects of heavy metal salts on concrete.

Nithya et al, [12] studied the effects of The Hydration of Heavy Metal Salts Admixtured High Alumina Cement (HAC). It was observed that heavy metal salts does not alter the compressive strength value very much except Zn added paste compared to HAC's value at the concentration of 2000ppm. The presence of Zn slightly accelerates the hydration reaction. This probably causes the setting time to decrease rapidly but the strength is found to be lower than control. This statement also supported by Murat and Sorrentino whereby the setting time of the mix containing Pb almost gives the same compressive strength value to control. Cr delayed setting time and lower strength than the control. An increase in Cr concentrations in HAC indicates a reduction in strength than control. The statement can be illustrated in Figure 2.

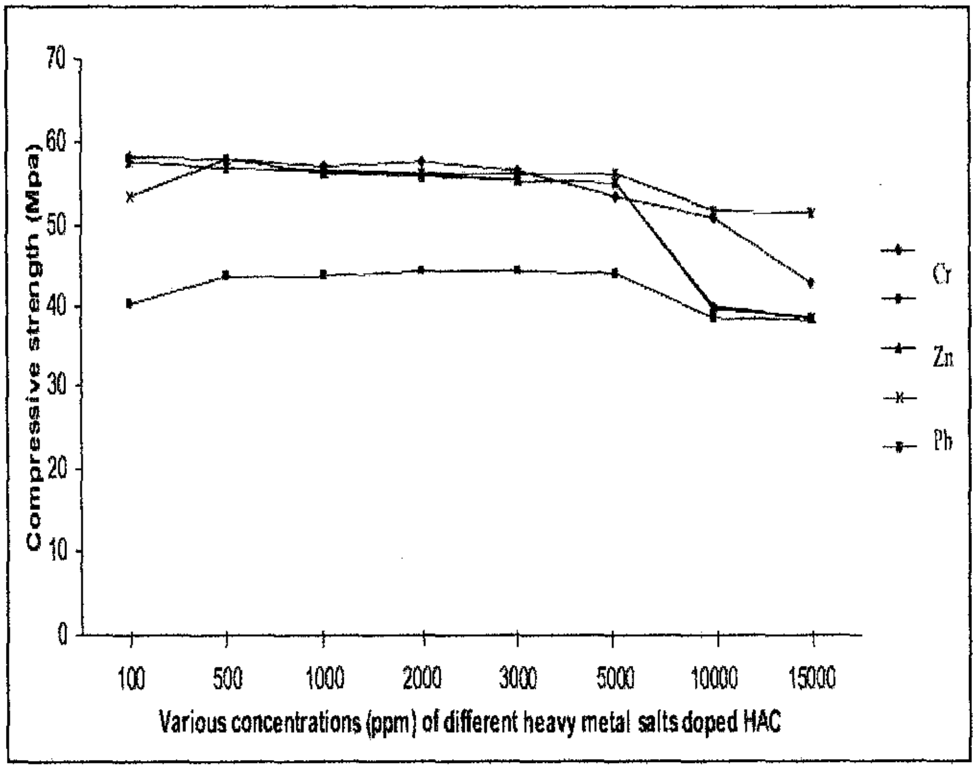


Figure 2: Compressive strength of heavy metal salts doped High Alumina Cement at 28th day by Nithya et al [12]

With the presence of lead the binder hydration occurred at a much slower rate and mortar mechanical strength was reduced. It is thought that coating of C_3S by metal ions or complex is responsible for the retardation. Immobilization of lead by hydraulic binders probably occurs by one or a combination of the following mechanisms:

Addition: C-S-H+Pb → Pb-C-S-H (1)

Substitution: C-S-H + Pb → Pb-S-H + calcium (2)

Precipitation of new compound: Pb + OH + Ca + SO4 → mixed salts (3)

Chatelet et al confirmed that Pb immobilization in calcium silicate hydrate (C-S-H) occurs as soon as C_3S begins to hydrolyze. The “Pb C-S-H” is referred as a C-S-H of regular stochiometry where lead replaces calcium.

2.3.3 Effects of phosphate on concrete

Effects of the presence of phosphate compound in concrete have been ambiguous. Small amounts of phosphorus pentoxide (P_2O_5) in the raw materials used for the manufacture of cement, can occur in some limestones, which can cause problems [4]. The content of P_2O_5 in most Portland cements is of the order of 0.2%; however, satisfactory cements can be manufactured from cement clinker containing up to 2.5% P_2O_5 by correct burning and proportioning, but the rate of hardening is slower. This is because the P_2O_5 decomposes C_3S forming a series of solid solutions between C_2S and $3CaO \bullet P_2O_5$. If larger amounts of P_2O_5 are present, free lime forms. If the lime content is reduced so that free CaO is is not formed, sound cements can be burnt from phosphatic raw materials but they develop strength more slowly because of the reduced C_3S: C_2S ratio. Thus, phosphate compounds also have been used as set retarders in concrete mixes.

Some inorganic salts (e.g., borates, phosphates, and zinc and lead salts) can act as retarders, but are not used commercially. Up to 500 ppm can generally be tolerated in mix water without causing significant set retardation. Basic research on the effect of retarders has shown that they slow down the rate of early hydration of C_3S by extending the length of the dormant period (i.e., second stage of hydration). Thus the setting time of Portland cement, as measured by the penetration test, is extended. The extension of the dormant period is proportional to the amount of retarding admixture used, and when the dosage exceeds a certain critical point, the C_3S hydration will never proceed beyond the dormant stage and the cement will not set. Sodium salts of phosphoric, boric, oxalic and hydrofluoric acid are soluble, but the calcium salts are high insoluble and therefore readily form in the vicinity of hydrating cement particles. Once insoluble and dense coatings are formed around cement grains, further hydration slows down considerably.

Phosphates are commonly found to be present as ingredients of commercial set-retarding admixtures and also have been used to produce a number of cement-based binders or phosphate-cements [13]. Although phosphate compounds have been sparingly used in concrete industry, there are reports indicating that phosphate compound containing engine oil was found as the cause for the scaling of airplane concrete parking apron. This however could be due to the decomposition of the organo phosphate compounds in the engine oil to phosphoric acids, which can cause disintegration of Portland cement matrices. On the other hand, findings by Naus et al [14] confirmed that there are no harmful interactions occur between phosphates solutions and hardened cementitious materials unless phosphates are present in the form of phosphoric acid.

2.3.4 Effects of chlorides on concrete

Sodium chloride was widely used to accelerate that set of Portland cement. Rixom and Mailvaganam [4] stated that the accelerating effect of calcium chloride on the set of Portland cement has been known since 1885. This effect, combined with the beneficial effect of calcium chloride on early strength development, resulted in its use either exclusively or as a major ingredient in accelerating admixtures for concrete

However, chloride ions when present in reinforced concrete can cause very severe corrosion of the steel reinforcement. The chloride ions will eventually reach the steel and then accumulate to beyond a certain concentration level. The protective film around the steel is destroyed and corrosion will begin when oxygen and moisture are present in the steel-concrete interface. Chlorides compounds can also react with cement matrices to form soluble salts such as calcium chloride that can leach away through pore waters [11].

Chlorides can originate from two main sources such as internal chloride and external chloride. Internal chloride is the chloride added to the concrete at the time of mixing including calcium chloride accelerators for rapid hardening concrete, salt contaminated aggregates and the use of sea water or other saline contaminated water. External chloride is chloride ingress into the concrete from environment. This category includes both de-icing salt as applied to many highway structures and marine salt, either directly from sea water in structures such as piers, or in the form of air-borne salt spray in structures adjacent to the coast.

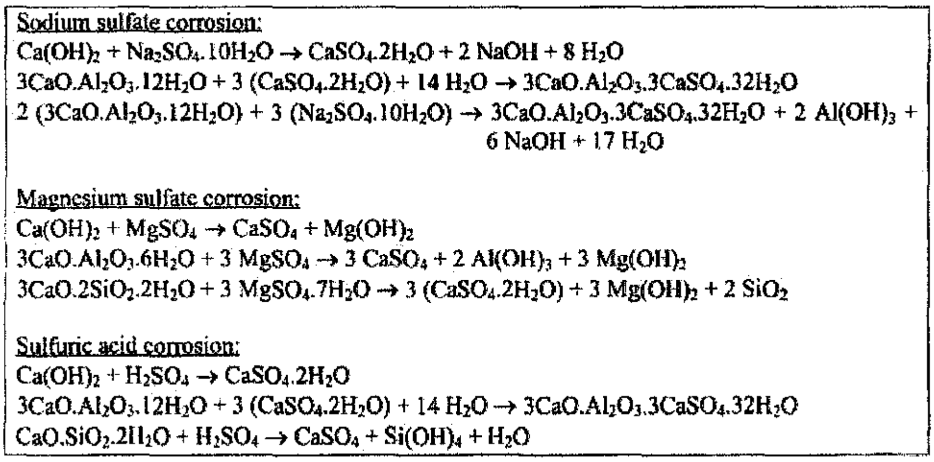
The effect of chloride salts depends to some extent on the method of addition. If the chloride is added at the time of mixing, the calcium aluminate (C_3A) within the cement paste will react with the chloride to some extent, chemically binding it to form calcium chloroaluminate. In this form, the chloride is insoluble in the pore fluid and is not available to take part in damaging corrosion reactions. The ability of the cement to chemically react with the chloride is however limited and depends on the type of cement. Arya et. al [4] stored ordinary Portland cement (OPC) and sulfate resistant Portland cement (SRPC) in a 20 g/l NaCl solution, and found that SRPC bound considerably less chloride than OPC, because of a lower C_3A content. It can be stated that higher C_3A content results in higher binding capacity.

2.3.5 Effects of sulphates and sulphuric acids on concrete

Sulphate attack normally results in expansion and cracking of concrete [11]. High sulphates content encourage formation of ettringite and gypsum. Although both exist in all portlandic concretes, excessive formation will cause cement matrices to expand and crack due to the building up of pressure. Concrete will lose strength and mass due to loss of cohesiveness of C-S-H gel, the principal cementitious constituent, as calcium hydroxide and C-S-H are converted into gypsum. Regarding sodium sulfate attack, the corrosive mechanism is divided into two parts. At low SO_4^{2-} concentrations (less than 1000 mg SO_4^{2-}/l), deterioration of the concrete is mainly due to the formation of ettringite. On the other hand, at high concentrations, the formation of gypsum is the main cause of deterioration [15, 16]. When gypsum is the main cause of deterioration, the tricalcium aluminate (C_3A) content of the cement is of less importance.

Sulphur oxides (SO_x) in contact with water also have been known to be capable of being oxidize into sulphuric acids when under certain atmospheric pressure and temperature. As main component of concrete exist in stable equilibrium in pore waters of high pH (12.5 to 13.5), contact with acidic ions of carbonates, sulphates and chlorides will have adverse effects on concrete [11]. Acid precipitation with a pH level ranging between 3.0 and 5.0 will affect cement and concrete. In the literature of J.Monteny (2000) [16], it was stated that the sulphuric acid reacts first with the calcium hydroxide ($Ca(OH)_2$) in the concrete to form gypsum. The formation of gypsum is associated with an increase in volume by a factor of 1.2±2.2. The reaction between gypsum and calcium aluminate hydrate (C_3A) with the formation of ettringite is said to be much more detrimental in hardened concrete, as volume of the ettringite mineral is several times greater than the volume of the initial compounds, with some reporting a 7 times increase in volume.

In an experiment using accelerated test establish in laboratory to investigate the effects of acid rain on the deterioration of cement concrete by Shaodong Xie et al (2004) [15], it is found that H^+ in sulphuric acid rain dissolves $Ca(OH)_2$ in the hardened cement paste and that SO_4^{2-} also corrodes it. The dissolution effect of H^+ will lead to the reduction of $Ca(OH)_2$ concentration in the concrete specimens. The corrosion of SO_4^{2-} produces the substances which are larger than $Ca(OH)_2$ in volume such as $Ca_3Al_6O_{12} \cdot CaSO4$ and $CaSO4 \cdot 2H2O$, leading to development of internal stress within inner part of the concrete specimen as a result of this volume expansion, which in turn resulting in significant decrease of the compressive strength of the concrete. The relationship between the reduction rate of strength, and CaO loss rate and the ratio of SO_3/CaO can be described as a binary linear correlation [15]. It has been found that acid rain causes chemical deterioration on carbonate stones such as marbles and limestone and formation of soluble Ca^{2+}, HCO_3^-, SO_4^{2-} and that dry deposition of SO_x, NO_x on the surface of stones contributes to salt enrichment on carbonate stones and plays a major role in the deposition of acid substances on buildings.



Sodium sulfate corrosion:

$Ca(OH)_2 + Na_2SO_4.10H_2O \rightarrow CaSO_4.2H_2O + 2\ NaOH + 8\ H_2O$

$3CaO.Al_2O_3.12H_2O + 3\ (CaSO_4.2H_2O) + 14\ H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$

$2\ (3CaO.Al_2O_3.12H_2O) + 3\ (Na_2SO_4.10H_2O) \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O + 2\ Al(OH)_3 + 6\ NaOH + 17\ H_2O$

Magnesium sulfate corrosion:

$Ca(OH)_2 + MgSO_4 \rightarrow CaSO_4 + Mg(OH)_2$

$3CaO.Al_2O_3.6H_2O + 3\ MgSO_4 \rightarrow 3\ CaSO_4 + 2\ Al(OH)_3 + 3\ Mg(OH)_2$

$3CaO.2SiO_2.2H_2O + 3\ MgSO_4.7H_2O \rightarrow 3\ (CaSO_4.2H_2O) + 3\ Mg(OH)_2 + 2\ SiO_2$

Sulfuric acid corrosion:

$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O$

$3CaO.Al_2O_3.12H_2O + 3\ (CaSO_4.2H_2O) + 14\ H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$

$CaO.SiO_2.2H_2O + H_2SO_4 \rightarrow CaSO_4 + Si(OH)_4 + H_2O$

Figure 3: Corrosion mechanism of sodium sulphate, magnesium sulphate and sulphuric acid [16].

While high concentration of sulphates are harmful to concrete, sulphates have also been found to be important to cement-admixture response, as sulphates inadequacy can suppress the silicate and aluminate hydration, which are important strength contributors to the concrete [10].

2.4 Treatment of UEO by Liquid-liquid Extraction method

Liquid-liquid extraction (LLE) is based on the transfer of a solute substance from one liquid phase into another liquid phase according to the solubility. Normally the solvent chosen is immiscible with the other solvent to allow easy phase separation. In the practical use, usually one phase is water or water-based (aqueous) solution and the other an organic solvent which is immiscible with water.

2.4.1 Ionic Liquids

Ionic liquids (ILs) are organic salts with melting points below 100°Celsius [19, 20, 21]. They are thermally stable, non-flammable, non-volatile, and demonstrate very low vapor pressure. Ionic liquids are soluble in a variety of organic and inorganic reagents. Hydrophilic ILs can also be highly water soluble. They have been employed extensively in Green Chemistry. As a powerful solvent, room temperature ionic liquids (RTILs) can dissolve a wide spectrum of organic, organometallic, and inorganic compounds Due to their low vapour pressure, there will be no loss of solvent through evaporation of IL, as opposed to the traditional organic solvents, which are usually VOCs that have high vapour pressure and low boiling point. Evaporation of organic solvents to the atmosphere is also one of the major causes of environmental pollution, as well as financial losses due to the loss of solvents. One of the most important advantages is that ionic liquids can be tuned/controlled by tailoring their cationic and anionic structures to optimize their physicochemical properties [19, 20, 21]. The miscibility of IL with water can be varied from complete miscibility to almost total immiscibility by changing the anion for example, Cl^- to $[PF_6]^-$. Similarly, the lipophilicity of the IL is modified by the degree of cation substitution. ILs can become more lipophilic with increasing alkyl substitution, resulting in increasing solubility of hydrocarbons and non-polar organics. [19]. RTILs have been studied to be used in the petroleum industry for selective extraction of impurities of oil products

2.4.2 Extraction of impurities by hydrophilic ionic liquids

ILs are considered to be polar solvents, but can be non-coordinating (mainly depending on the IL's anion) [19]. Solvatochromatic studies indicate that ILs have polarities similar to those of short-chain alcohols and other polar, aprotic solvents, that is the polarities are between water and chlorinated organic solvents and varies, depending on the nature of the IL components.

ILs tend to be immiscible with alkanes and other non-polar organic solvents and hence can be used in two-phase systems. Similarly, it is possible to design ILs that are hydrophobic and can be used in aqueous/IL biphasic systems [19]. Therefore, accordingly, most ILs are capable of extracting ionic compounds from oil when mixed with the oil due to the more polar nature of IL than oil, and then be separated from the oil due to immiscibility. ILs should settle to the bottom of the biphasic system with oil at the top due to difference of their densities. However the rate/effectiveness for extraction is a complex matter and will be dependent on the compatibility of the chemical structure properties of the ILs and the ionic compounds. Some ILs even extract some organic and hydrocarbon components from the oil.

In one of the examples, Dishun Zhao et al [20] shows successful desulfurization of fuel oil by oxidization of sulphur components and extraction of them by using *N*-butyl-pyridinium-based IL ([BPy]BF4) and hydrogen peroxide. Experiment was carried out shows optimum extraction achieved at V(IL)/V(Oil) /V(H_2O_2) = 1:1:0.4, temperature 55 °C, the time 30 min. The ratio of desulfurization to thiophene and DBT (organo sulphates) reached 78.5% and 84.3% respectively. In this case, extraction happen as H_2O_2 oxidizes thiophene sulphides to the corresponding sulfone, which eventually remained in the IL phase due to the polarity.

As the concrete damaging impurities of UEO are assumed not to consist of organic compounds, the extraction process should be quite straight forward, where significant amount heavy metal salts, sulphates, phosphates and chlorides will be extracted to the IL phase through polarity. Efficient extraction of the aforementioned critical components will open new path to better contribution of concrete performance by treated UEO

3. METHODOLOGY

In this chapter, all procedures and experimental methods of this project are thoroughly explained. There are 4 sub-chapters, which are:

1. Collection of UEO samples.
2. Chemical analysis of UEO samples.
3. Treatment of UEO through Liquid/liquid extraction (LLE) by ionic liquids.
4. Concrete Testing.

3.1 Collection of UEO samples

The objective of the project is to determine the effects of different UEO on concrete, as there are many different brands of engine oil with different type of base oil and additives packages. Engine oil that has gone through different combustion engine and length of usage also will have different impurities. Thus it is important to obtaining different UEO from different sources for variety and comparison purposes later in the research.

The first phase of this experiment is the collection of different UEO samples. Samples of UEO are collected from 5 different service stations in Ipoh, namely Toyota service station, Perodua service station, a mechanic shop, a lorry service station diesel engine oil, and a motorcycle service station. The 5 samples are named as: Toyota, Perodua, Random, Diesel, and Motor. The purpose of this sample collection pattern is to obtain different types of UEO from different sources that are available at the present.

3.2 Chemical analysis of UEO samples

The second phase of this experiment involves chemical analysis of the UEO samples by XRF qualitative analysis, density test and pH test.

3.2.1 X-Ray fluorescence (XRF) Qualitative Analyis

Impurities of the UEO are known to consist of various metal oxides, phosphates, sulphates and chlorides. Qualitative analysis approach of the UEO is done by using the X-Ray fluorescence (XRF), equipment of the Mechanical Department. The analysis by XRF is to identify the main chemical compounds/components in the UEO, namely magnesium, sulphate, phosphate, chloride and possibly other metals (vanadium, zinc, iron, lead) and the rough percentage of each of the chemical components in the UEO samples. Samples of UEO that have been treated by ILs (TUEO) are also sent for another XRF analysis. The percentage of each chemical impurities will provide information for making any hypothesis regarding the reasons behind results.

3.2.2 Density test and pH test

Besides XRF, pH test of the UEO and TUEO have been carried out to see whether any acids exist in the UEO or not. Density and viscosity test of the UEO will be conducted by using the density meter (DMA 5000M) and viscosity meter (Starbinger) in the Petronas Ionic Liquid Centre (PILC). The reason for the density and viscosity test is to identify the original density and the viscosity of the UEO, which will be compared to the established standards for lubricant oil, such as the American Petroleum Institute (API) standard. The treated UEO (after chemical extraction by IL) will also undergo the density and viscosity test. The values will then be compared to the density and viscosity of the untreated UEO to check the suitability of the IL for chemical extraction in UEO. This is because the ILs, which are powerful solvents tend to extract some hydrocarbon chains from oil. If large quantity of hydrocarbon is dissolved in the IL, it will be indicated in the density values, where there will be large value difference between the untreated UEO and the treated UEO.

3.3 Extraction of UEO impurities by ionic liquids

In this phase, there are two stages of work. In the first stage, small scale lab testing will be carried out, with each five ILs tested with UEO samples. Second stage, large scale treatment of UEO will be carried out for concrete testing purposes.

3.3.1 Small scale lab testing/treatment

The purpose of this small scale lab testing is to identify the best IL available for extracting ionic impurities from the UEO. Determination of the type of ionic liquid to be used is based on the availability of the ionic liquid in the PILC lab. In this experiment, 2-hydroxyethyl ammonium formate (HEF), bis(2-hydroxylethyl) methyl ammonium formate (BHEF), 2-hydroxyethyl ammonium acetate (HEA), 1-n-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]), and 1-butyl-3-methylimidazolium acetate ([bmim][Ac]) were used. The hydroxyl ammonium ionic liquids were synthesized by a phD student in PILC. It was said that the hydroxyl ammonium ionic liquids are one of the cheapest ionic liquids in the world. The tests are conducted at small scale to minimize the cost of the experiment and to avoid wastage of the ILs, since some ILs are very expensive and precious. The lab testing in this project is conducted by mixing UEO and IL at 1:1 scale, where 5 grams of each of the UEO samples will be mixed with 5 grams of selected IL respectively. HEF was the first to be experimented.

After mixing the each of the UEO samples with the HEF in 5 separate bottles at 1:1 scale, the mixture will be stirred at 500 RPM for 30 minutes to achieve a homogenous phase. After that, the bottles are left aside for 3 days for gravitational settlement/separation of the mixture into two phases of liquid, with UEO phase on top of the HEF phase. Treated UEO at the top will then be separated by a pipette and sent for XRF analysis. The ionic impurities in the treated UEO sample will be compared to the amount of the ionic impurities in the untreated UEO. Density test and pH test are also carried out on the TUEO.

Other ILs, namely BHEF, HEA, BmimSCN, BmimAC, are also tested with the same procedure. Due to limited amount of the BmimSCN and BmimAC, the test of BmimSCN was only done with Perodua sample, while BmimAC was only tested with Diesel sample.

Criteria for the determining the suitability of ILs in this experiment is achieving phase separation or partitioning between the ILs and UEOs.

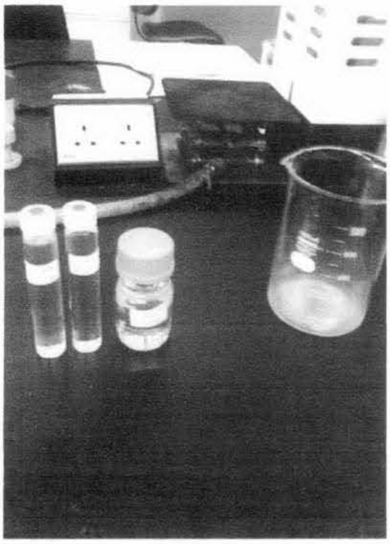


Figure 4: Toulene and hexane, which are used for dissolving UEO and for cleaning of apparatus.

Figure 5: 5 grams of UEO and 5 grams of IL (HEF) are carefully measured and placed in a bottle, which are then sent for centrifuging at 500 rpm for 30 mintues.

Figure 6: Mixtures in bottles are left to settle into two phases for 18 hours. The picture shows the two phases of UEO and IL after settlement. From left: Motor, Diesel, Toyota, Random, Perodua. From first glance, the HEF dissolve about 30% of the hydrocarbons in the UEO.

Figure 7: T UEO samples were extracted by a pipette and placed in vials. The samples are then sent for XRF analysis.

3.3.2 Large scale treatment

In the second stage of the experiment, large scale treatment of the UEO was carried out. The type of the IL will be determined by the tests from the first stage. The treated UEO from this stage will be used as concrete admixture in the concrete testing phase. The procedure of this stage is same as the small scale testing, except that UEO and IL used will be larger in volume, with 35 grams of each five UEO samples mixed with 35 grams of HEF in 5 separate beakers respectively. In this treatment process only HEF is used due to its better overall phase separation. Only Motor sample is left out due to poor phase separation. Mixtures in four separate beakers were stirred at 500RPM for 30 minutes and then left aside for 3 days. After 3 days, all the TUEO phases on top of the HEF phases is extracted using a pipette.

3.4 Concrete testing

In this phase, concrete mixes with different UEO and TUEO as admixture are tested for workability (slump test), 28-days compressive strength and porosity. Each test will be carried out following the standard procedure (refer to UTP Concrete Lab Procedure).

In this project, concrete mixes with design strength of 30MPa is used. The following is the general mix proportion:

MIX	**w/b**	**UEO (Admixture)**	**Cement (kg/m^3)**	**Fine Agg (kg/m^3)**	**Coarse Agg. (kg/m3)**
OPC	0.55	0.5%	325	757.3	1137.5

Quantity of admixture (UEO and TUEO) to be used is 0.5% of the cement weight, as it was found by Beddu et al [4] to be the optimum amount. A total of 10 concrete mixes of different admixture were made. The concrete mixes consist of each of the 5 untreated samples of the UEO as admixture, and also 4 TUEO. There was no TUEO of Motor sample due to the poor phase separation from HEF. The following are the list of concrete mixes to be made:

Concrete mixes	Concrete admixture (0.5% weight of cement)
Control Mix (CM)	None
UEO-T	UEO - Toyota
UEO-P	UEO – Perodua
UEO-R	UEO - Random
UEO-D	UEO – Diesel
UEO-M	UEO – Motor.
TUEO-T	Treated UEO – Toyota
TUEO-P	Treated UEO - Perodua
TUEO-R	Treated UEO – Random
TUEO-D	Treated UEO – Diesel

Table 1: Concrete mixes made

For each concrete mixes, Slump test, compressive strength test and porosity test are carried out. Volume mixed for each mixes are determined through a series of calculation shown in Appendix I.

3.4.1 Slump test

Slump tests are carried out right after the mixing of the concrete. Concrete are mixed by using a mixer, which drum surface are wetted prior to mixing. Aggregates (fine and coarse) are then mixed for approximately 1 minute until they are thoroughly mix. Cement are added later and mixed for another 1 minute until it is thoroughlt mixed with the aggregates. Half of the water is added and the mixture are mixed for 2 minutes. After 2 minutes, the remaining water is added and mixed for another 3 minutes. The total mixing time after addition of water is 5 minutes. Admixtures (UEO or TUEO) are added after 3 minutes of addition of water.

Slump test are carried out on the 6th minute, right after the 5 minutes of mixing. The slump cone used is of standard size, with 20-cm diameter base. 10 cm diameter top and 30 cm in height. The cone is filled with 4 equal layers of concrete, each layer tamp for 25 times by a tamping rod. Top surface is then levelled off. The cone was then slowly lifted upwards, and put beside the slumped concrete. The slump achieved is measured, which is the height difference of the slumped concrete and the cone.

3.4.2 Compressive strength test

Three cubes of 100mm×100mm×100mm concrete are made for each different mixes. Each steel moulds are filled by two layers, each layers tamped by tamping rod for 25 times. Top surfaces are levelled off with a trowel. After 24 hours, the moulds are open and the cubes are cured in a water tank. Compressive strength of each cubes are tested 28 days after mixing.

3.4.3 Porosity test

In this project, the porosity of the concrete is tested by the vacuum saturation method. A concrete slab with dimension of 150mm×25mm×50mm is made for each different concrete mixes. After 28 days of curing, slab is cored into three 50mm diameter cylinders using a coring machine in Petrolem & Geosciene Department.

Cylinders are naturally dried for 24 hours. Then they were placed on top of a perforated plate in a vacuum glass container. This is to allow better circulation to the bottom of the concrete cylinders. The container is closed with the lid that is connected to a vacuum pump. The container is then vacuumed for 30 minutes.

After 30 minutes, vacuum is switched off and the glass container is filled with water until all the concrete cylinders are submerged. The container is then close with the lid and vacuumed for another 6 hours. After 6 hours, the now saturated concrete cylinders are weighted. The weight of the saturated sample in air and in water is recorded.

After recording the weight of samples both in air and in water, the samples are placed in oven to be dried for 24 hours at 110°C. After 24 hours, the oven-dried samples are then weighted again. The porosity of the concrete is calculated with the following formula:

$$Porosity = \left(\frac{Wa - Wd}{Wa - Ww}\right) \times 100\%$$

Where,

Wa = Saturated concrete weight in air

Ww = Saturated concrete weight in water

Wd = Oven-dried concrete weight in air

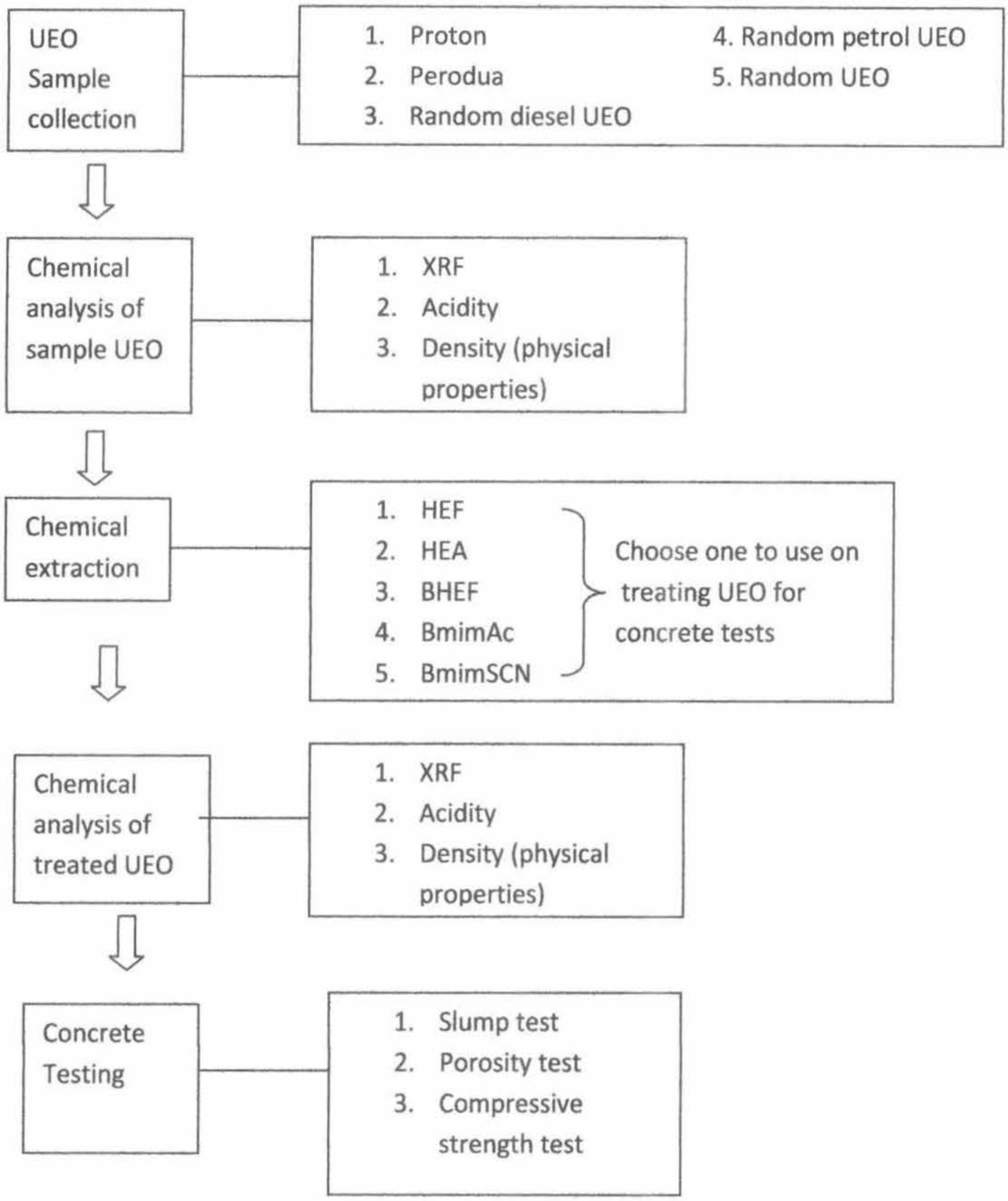


Figure 8: Flowchart of project procedures

4. RESULTS AND DISCUSSIONS

In this chapter, results from the experiment and findings following the project methodology are rigorously interpreted and discussed. The sub-chapters are arranged in accordance to the flow of the methodology, to discuss each process, interpret results and findings, as well as discussing any flaws in any part the methodology. Titles of the sub-chapters are: Extraction of UEO impurities by ionic liquid, Chemical analysis of UEO and TUEO treated by HEF and Concrete Testing.

4.1 Extraction of UEO impurities by ionic liquid

The following shows the results and findings on small scale lab testing using the five different ionic liquid, namely 2-hydroxyethyl ammonium formate (HEF), bis(2-hydroxylethyl) methyl ammonium formate (BHEF), 2-hydroxyethyl ammonium acetate (HEA), 1-n-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]), and 1-butyl-3-methylimidazolium acetate ([bmim][Ac]), on various UEO samples.

During the small scale lab testing, it was noticed that many UEO did not have clear partitioning or phase separation with the ionic liquids. As clear phase separation is important to allow easy separation of treated UEO (TUEO) from the ionic liquid phase, it is the first criteria in determining the suitability of an ionic liquid to be used for treatment/extraction of UEO impurities purposes.

Due to the poor separation, water is added to the mixture to help separating the UEO from ionic liquids. Water:UEO:ionic liquid ratio is 1:1:1. In theory, water is immiscible with oil, while all the hydroxyl ammonium IL used in this project are hydrophilic. Thus, water is used as a solvent to extract IL from the UEO, leaving behind two clear phases, where UEO phase is on top and IL+water phase at the bottom due to density differences.

4.1.1 HEF testing

Before addition of water

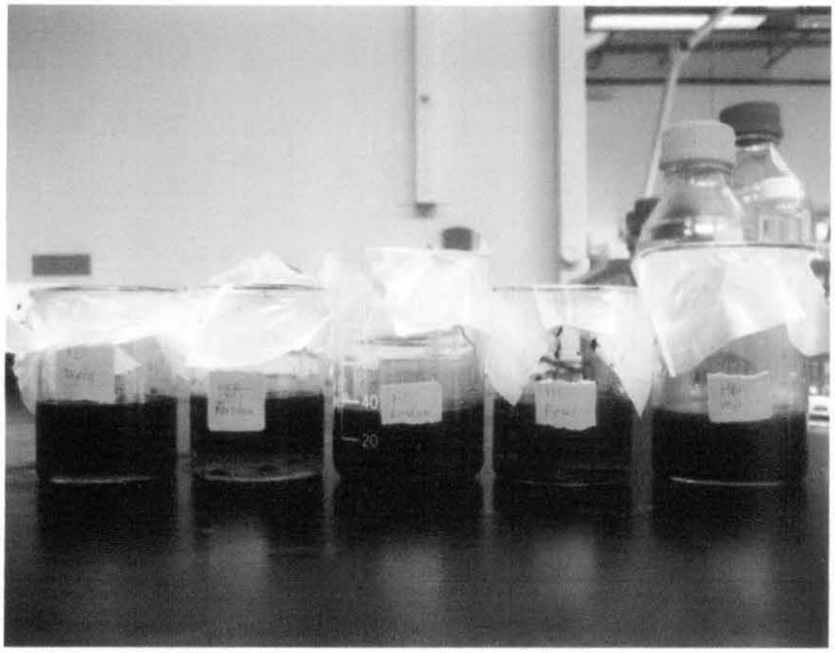


Figure 9: UEO + HEF after being left for separation for 3 days. From the left is Toyota, Perodua, Random, Diesel, Motor.

1. HEF + Toyota had separated into two clear phases after 3 days. Colour of the HEF became dark brown. The Toyota phase had became less than before, which could be due to the cross-solubility of some hydrocarbons into the HEF phase.
2. HEF + Perodua had separated but without clear separation line between the two phases after 3 days. This may be due to due to the cross-solubility of some hydrocarbons into the HEF phase, or slow settlement of the HEF. Colour of HEF became brown.
3. HEF + Random had separated but without clear separation line between the two phases after 3 days. This may be due to due to the cross-solubility of some hydrocarbons into the HEF phase, or slow settlement of the HEF. Colour of the HEF Colour of HEF became dark brown.
4. HEF + Diesel had separated into two clear phases after 3 days. The colour of the HEF became slightly darker.
5. HEF + Motor had separated into two clear phases after 3 days. However the Motor phase had drastically reduced, which could be due to high cross-solubility of hydrocarbons into the HEF phase, or due to the slow separation rate. Colour of HEF became dark grey

After addition of water

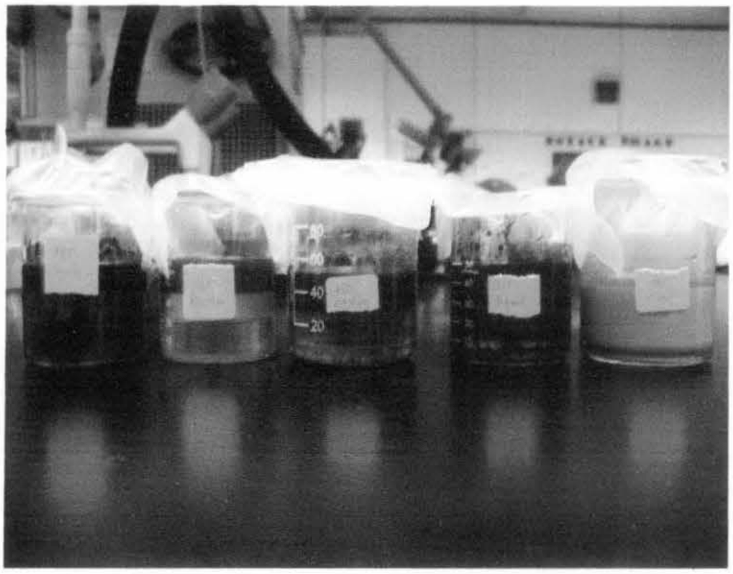


Figure 10: UEO + HEF stirred with water after 3 days being left for separation. From the left is Toyota, Perodua, Random, Diesel, Motor.

1. HEF + Toyota + Water had separated into two clear phases after 3 days. The HEF + water phase is dark brown in colour.
2. HEF + Perodua + Water had separated into 3 phases, UEO at the top, UEO + HEF + Water Emulsion in the middle, and HEF + Water at the bottom. The UEO has turned lighter in colour. The emulsion phase is light brown and foamy. HEF + Water is yellowish in colour.
3. HEF + Random + Water had separated separated into two clear phases after 3 days. The HEF + Water phase is brownish in colour.
4. HEF + Diesel + Water had separated into two clear phases after 3 days. The HEF + Water phase is slightly yellowish in colour.
5. HEF + Motor + Water are mixed into a emulsion which is light brown in colour. A very thin layer of very light coloured oil phase is visible on top of the emulsion.

It is noticed after addition of water, foams/emulsions are visible. These emulsions are believed to be complex salts that formed after reaction, and then suspended in oil and water emulsions. The reduction of volume in TUEO phases when compared to UEO is also visible (Levels of UEO were marked by stickers). This may be due to some hydrocarbons and impurities of the UEO crossing into the IL phase.

4.1.2 HEA testing

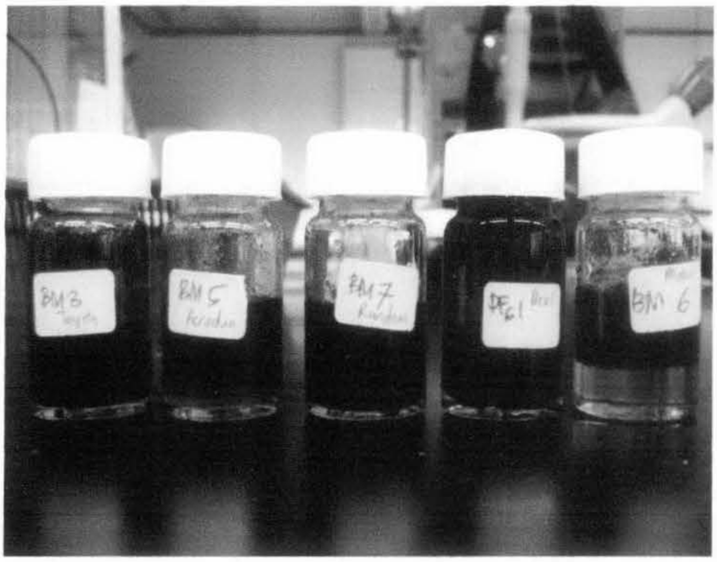


Figure 11: UEO + HEA being left for separation for 3 days. From the left is Toyota, Perodua, Random, Diesel, Motor.

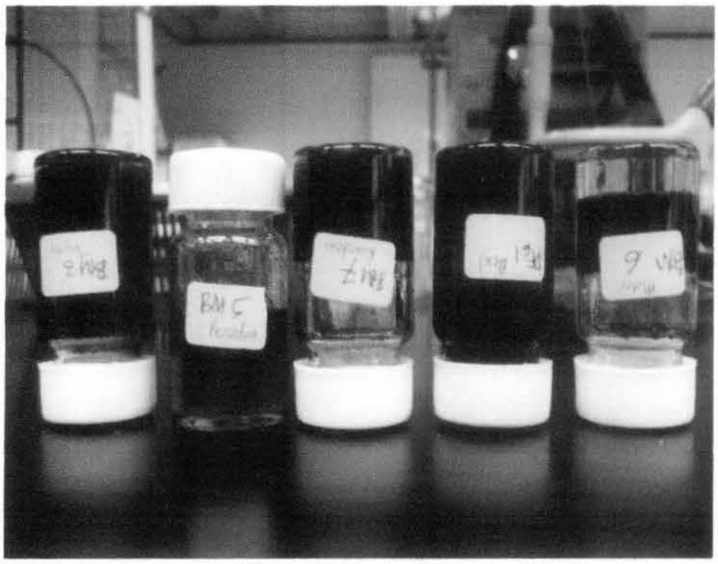


Figure 12: Four of the UEO + HEA except HEA + Perodua have solidified into gels. From the left is Toyota, Perodua, Random, Diesel, Motor.

*Four mixture samples were solidified into gel form after 3 days. Only HEA + Perodua remains liquefied.

1. HEA + Toyota and HEA + Diesel mixtures had not separated into two phases after 3 days.
2. HEA + Perodua had separated but without clear separation line between the two phases after 3 days.
3. HEA + Motor had separated into two clear phases, but is solidified.
4. HEA + Random had separated into two clear phases which is only visible with camera flash, or under UV light.

4.1.3 BHEF testing

Before addition of water

Figure 13: UEO + BHEF being left for separation for 3 days. From the left is Toyota, Perodua, Random, Diesel, Motor.

1. BHEF + Toyota, BHEF + Perodua and BHEF + Random mixtures had not separated into two phases after 3 days.
2. BHEF + Diesel mixtures separated into two phases. The ionic liquid phase colour has not changed much.
3. BHEF + Motor mixtures separated into two phases. The ionic liquid phase colour has changed into dark grey.

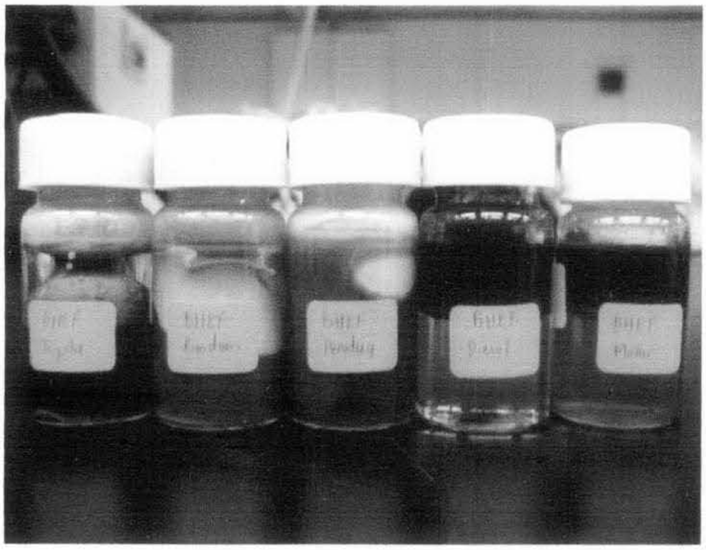


Figure 14: UEO + BHEF stirred with water after 3 days being left for separation. From the left is Toyota, Perodua, Random, Diesel, Motor.

After addition of water

1. BHEF + Toyota + Water had formed emulsion. Water has seen to be on top of the black coloured emulsion phase.
2. BHEF + Random + Water and BHEF + Perodua + Water had formed brownish, foamy emulsion that cannot be separated.
3. BHEF + Diesel + Water had separated into two clear phases: with UEO phase on top of the ionic liquid + water phase. The ionic liquid + water phase is clear and colourless.
4. BHEF + Motor + Water had separated into two clear phases: with UEO phase on top of the ionic liquid + water phase. The ionic liquid + water phase is brownish in colour.

4.1.4 BmimAc & BmimSCN testing

These two imidazolium ionic liquids were initially purchased from MERCK by a PILC phD student. Due to the cost and limited amount of the imidazolium ionic liquids, only one sample is tested for each of the imidazolium ionic liquids: BmimAc + Diesel and BmimSCN + Perodua.

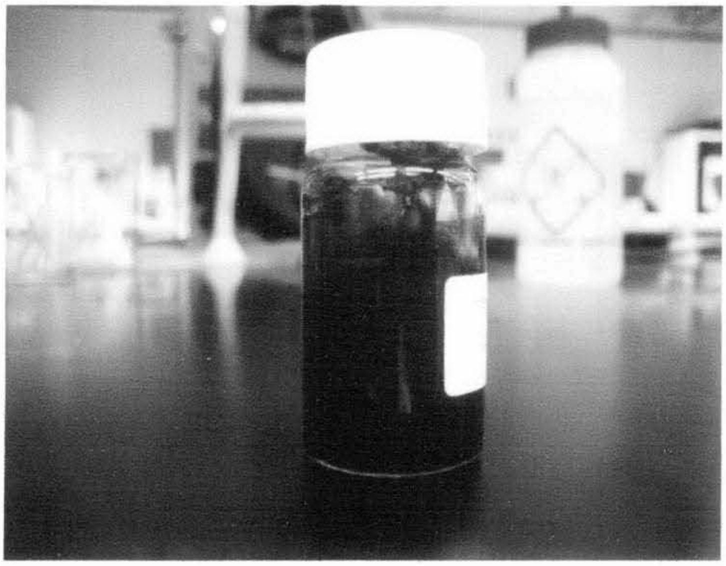


Figure 15: BmimAc + Diesel after 3 days being left for separation.

1. BmimAc + Diesel had not separated after 3 days and remains in one phase.

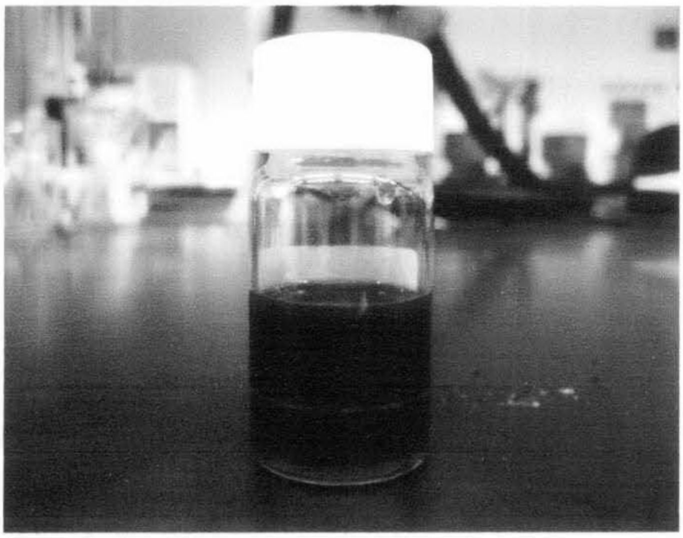


Figure 16: BmimSCN + Perodua after 3 days being left for separation.

2. BmimSCN + Perodua had completely separated after 3 days into two clear phases. The UEO phase has became lighter in colour, while the ionic liquid phase has turned darker in colour.

<u>After addition of water</u>

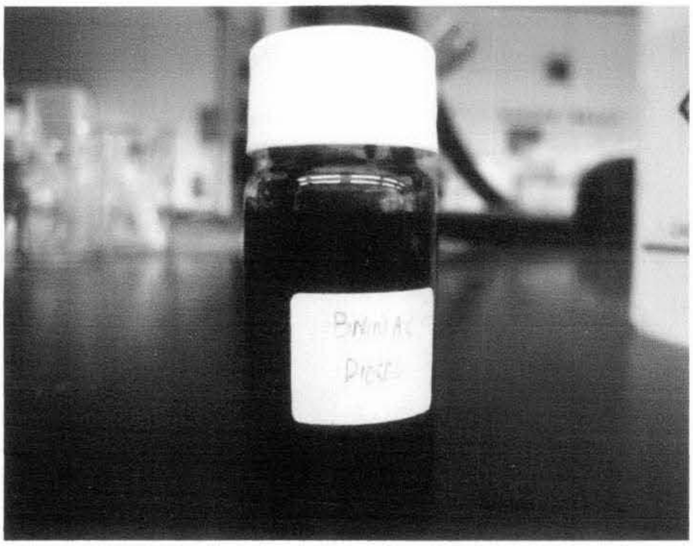


Figure 17: BmimAc + Diesel + Water after 3 days being left for separation.

3. BmimAc + Diesel + Water had not separated after 3 days and remains as one phase. This may be due to the high quantity of aromatics in the Diesel sample, which have high solubility in the imidazolium ionic liquids, which have aromatic cations.

It is noticed that not all UEO+IL mixture achieved phase separation, however the potential of using IL as LLE solvent can be seen with some successful phase separation.

4.1.5 UEO treatment by HEF for Concrete Tests

To produce sufficient treated UEO (TUEO) for the concrete tests, a considerably large amount of ionic liquid is required. As total volume of concrete per mix is calculated to be 16 litres, each mix will require 26 g of admixture (UEO and TUEO). This would mean at least 150 g of ionic liquid is required (at least 30 g for each of the five UEO samples), with the additions to compensate errors, wastage, and also loss of UEO hydrocarbons due to cross-solubility into ionic liquids. This would mean that the immidazolium ionic liquids of BmimAc and Bmim SCN given (approximately 10 g each) are far too less to be used for mass-treating for concrete purposes.

On the other hand, the for the hydroxyl ammonium ionic liquids, HEF have given better separation results than its counterparts, HEA and BHEF. Also, hydroxyl ammonium ionic liquids are considerably abundant as they were synthesized by Dr.Kiki of PETRONAS Ionic Liquid Centre (PILC). It was also said that the precursors to synthesizing hydroxyl ammonium ionic liquids are significantly cheaper than immidazolium ionic liquids, thus making hydroxyl ammonium IL one of the cheapest IL in the world. Due to that, HEF is chosen to be used for treating UEO samples for concrete test.

	Toyota	Perodua	Random	Diesel	Motor
HEF	Good	Average	Average	Good	Poor
HEA	-solidified - inseparable	Poor	-solidified - inseparable	-solidified -inseparable	solidified
BHEF	inseparable	inseparable	inseparable	Good	Good
BmimAC	N/A	N/A	N/A	inseparable	N/A
BmimSCN	N/A	Good	N/A	N/A	N/A

Table 2: Ionic liquids phase separation performance as summarized, after mixing with UEO samples. HEF is chosen for large scale treatment of UEO for concrete tests.

Treatment process is same as the initial small scale testing, with ionic liquid to UEO ratio of 1:1, except that the scale in this work is larger.

4.2 Chemical Analysis of UEO and TUEO treated by HEF

This sub-chapter will discuss the XRF qualitative analysis results, density test of TUEO treated by HEF, and pH test of the UEO and TUEO.

4.2.1 XRF qualitative analysis results

XRF analysis results for each UEO samples and TUEO treated by HEF are shown in the Table 3 below. This XRF analysis was just a qualitative analysis and not a quantitative analysis, as the XRF machine has not been calibrated by certified standard solutions containing the impurities found in UEO. Although this XRF analysis was just a qualitative analysis, where accurate concentration of the impurities in UEO and TUEO is not known, rough estimation of the removal rate of the impurities in TUEO by HEF can be calculated by the following formula:

$$Removal\ rate, \% = \left(\frac{\%UEO - \%TUEO}{\%UEO}\right) \times 100$$

Where

%UEO = the percentage of each compound in UEO

%TUEO = the percentage of each compound in TUEO

It is found that the removal rates of SO_3, CaO, ZnO and MgO by the HEF were very good, where removal rates are in the range of 50%-100%. On the other hand, removal rates of P_2O_5, Fe2O3 and CuO were not too good, where removal rates are only between 0%-35%.

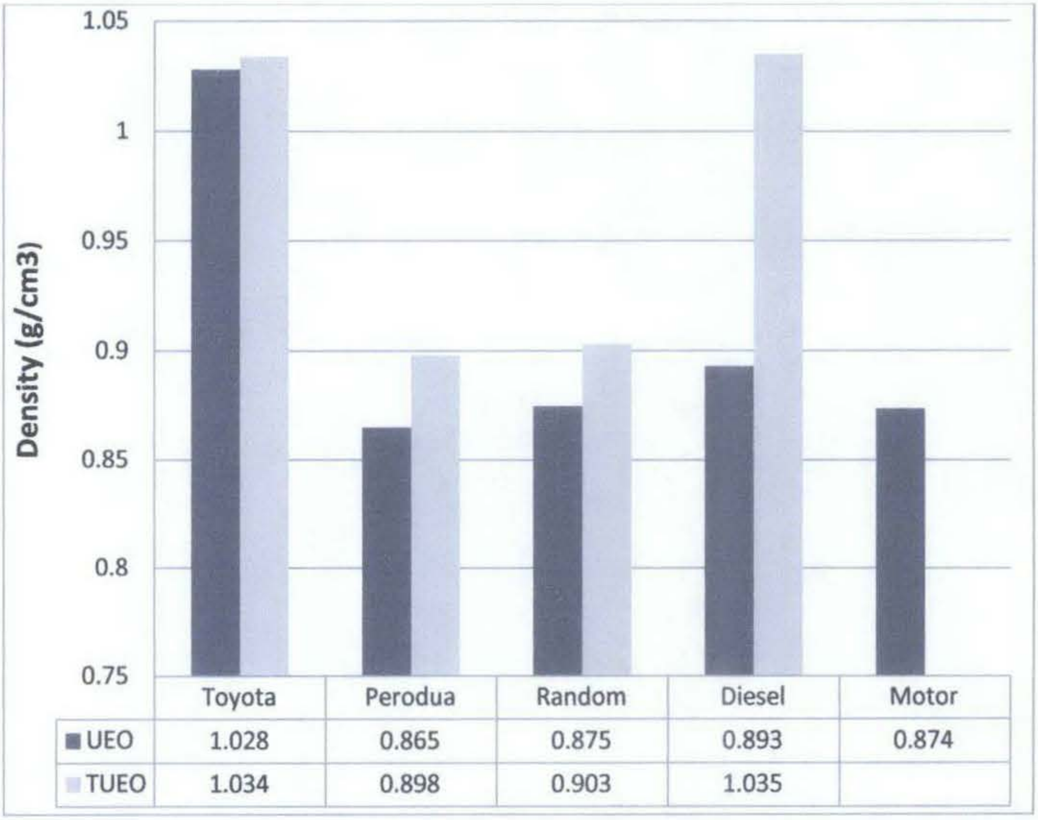
			P2O5	SO3	CaO	Fe2O3	CuO	ZnO	MgO
Toyota	UEO	KCps	3.7	24.3	15.8	4.3	2.3	18.9	-
		%	14.7	61.5	20.1	1.29	0.3	2.08	-
	TUEO	KCps	3	9.6	3.8	4.1	2	2.5	-
		%	14.06	31.19	5.71	1.29	0.3	0.3	-
		Removal rate (%)	4.35	49.28	71.6	-	-	85.58	-
Perodua	UEO	KCps	5.8	51	21.1	4.9	3.8	48.6	-
		%	12.6	69.09	14.8	0.719	0.237	2.65	-
	TUEO	KCps	3.6	21	4.8	3.6	2	-	-
		%	11.02	43.02	4.97	0.719	0.19	-	-
		Removal rate (%)	12.54	37.73	66.42	-	19.83	100	-
Random petrol	UEO	KCps	4.1	12	14.4	3.8	2	20.3	-
		%	23.4	45.7	25.4	1.72	0.37	3.44	-
	TUEO	KCps	2.8	1	4.2	3.4	2	6.8	-
		%	16.37	4.32	7	1.46	0.37	1.21	-
		Removal rate (%)	30.04	90.55	72.44	15.12	-	64.83	-
Diesel	UEO	KCps	5.2	56.9	23.8	10.7	2	26.9	-
		%	10.5	70.81	15.7	1.56	0.3	1.41	-
	TUEO	KCps	2.8	1.7	4.2	3.8	1.8	9.9	-
		%	10.5	4.65	4.41	0.97	0.22	1.05	-
		Removal rate (%)	-	93.43	71.91	37.82	26.67	25.53	-
Motor	UEO	KCps	6.3	27.4	20.5	5.1	-	40.7	0.4
		%	19	52.8	18.5	1.05	-	3.09	5.5
	TUEO	KCps	3.6	9.1	6.7	3.4	-	2.9	-
		%	14.73	18.15	8.82	1.05	-	0.31	-
		Removal rate (%)	22.47	65.63	52.32	-	-	90	100

Table 3: XRF results of each UEO and TUEO sample treated by HEF and removal rates of the impurities

4.2.2 Density test results

It can be seen in Figure 17 below that difference of density between Toyota TUEO and Toyota UEO is the smallest, indicating very good phase separation between HEF and Toyota TUEO. It also indicates that there are very small amount of IL crossing into the UEO phase. Similarly, densities of TUEO of Perodua and Random are slightly higher compared to their UEO counterparts. TUEO of Diesel has density that is significantly higher than its UEO counterpart. This indicates the high amount of IL that crossed into the UEO phase, which is also observed in the increased volume of Diesel TUEO phase in the bottle.

The reason for density of TUEO treated by HEF are higher than the density of UEO is because of cross-solubility between IL phase and UEO phase, where some IL are crossed and left in the UEO phase. There may also be chemical reaction between the impurities, UEO and added water, leaving behind a heavier/denser complex salt in TUEO, thus the higher density than UEO.



	Toyota	Perodua	Random	Diesel	Motor
■ UEO	1.028	0.865	0.875	0.893	0.874
□ TUEO	1.034	0.898	0.903	1.035	

Figure 18: Density of TUEO treated by HEF compared to UEO.

4.2.3 pH test results

This test is to check the pH values of the UEO and TUEO treated by HEF. It was predicted in the literature review that UEO can be acidic when all the buffers, which neutralize acids in the lubricant are used up. Acids exist in UEO due to the oxidization of SO_3 and P_2O_5 under high pressure and temperature of the internal combustion engine. SO_3 and P_2O_5 can also be oxidized into acids when in contact with water. P_2O_5 is sparingly soluble in water and form phosphoric acid, H_3PO_4. In Table 4 shown below, Perodua and Random UEO are tested to be acidic, with pH of 6.53 and 6.01 respectively. This has verified the existence of acids in certain UEO.

Acids can cause deleterious effects on concrete hardened properties, especially strength wise. Part of the objective of the treatment of UEO is to remove or neutralize these acids to create a more benign UEO for concrete. Unfortunately, pH test on Perodua, Random and Diesel TUEO shows much lower pH values, that is 5.55, 4.5, and 3.65 respectively. This may be due to some chemical reaction between the IL, water, and UEO impurities that releases acids, causing the increase in acidity. Thus, this is a first indication that HEF may not be suitable for treating UEO.

	pH values	
	UEO	TUEO
Toyota	7.12	7.24
Perodua	6.53	5.55
Random	6.01	4.5
Diesel	7.28	7.16
Motor	7.07	N/A

Table 4: pH of TUEO compared to UEO

4.3 Concrete tests

Due to limited stock of ionic liquids and liquid phase separation problems, only UEOs treated with HEF are used for concrete tests. As the Motor sample treated by HEF failed to separate successfully (too little amount of oil recovered), Motor TUEO sample is discarded from concrete tests. Concrete test samples with untreated UEO are named UEO Toyota, UEO Perodua, UEO Random, UEO Diesel and UEO Motor. On the other hand, samples with treated UEO are named TUEO Toyota, TUEO, Perodua, TUEO Random and TUEO Diesel.

4.3.1 Slump test results

Slump tests are carried out right after the end of mixing. Admixtures are added 3 minutes after the addition of water. Mixings are ended 5 minutes after the addition of water. Slump of Control mix achieved is 30mm.

It is notice that most UEO increase the slump by 50% - 70% when compared to control mix. Random UEO increase the slump by 200%. On the other hand Perodua UEO did not increase the slump. The reason that concrete with admixtures (UEO and TUEO) give higher slump could be due to lubricating and dispersing effect of oil on the aggregates and cement. Impurities such as P_2O_5, SO_3 and ZnO could have also affected the slump. P_2O_5 are sparing soluble and capable of forming phosphates, which can retard the setting time of cement, as well as retarding the hydration of the cement matrices, thus contributing to the improvement of workability. Sulphonates or compounds with SO_2 anion have been found as main ingredient of super-plasticizer, thus SO_3 could have also contributed to the dispersing effect. On the other hand, ZnO can accelerate hydration of cement paste, causing the setting time to be shorter and resulting in lower workability and decreased hardened concrete strength.

TUEO gives more or less the same amount of slump compared to the UEO. Slumps of UEO and TUEO Toyota were equal. Slumps of TUEO Perodua and Random are slightly lower than their UEO counterparts, while slump of TUEO Diesel is slightly higher than its UEO counterpart.

These findings that show little differences between UEO and TUEO slumps, could also be a hint that the plasticizing effect or dispersing capabilities of the UEO may be more dependent of the base oil of the UEO than its impurities.

The following table shows the results of slump test with Untreated UEO compared to Treated UEO:

Admixture	**UEO**	**TUEO**
Toyota	50	50
Perodua	30	25
Random	95	70
Diesel	40	50
Motor	45	N/A

Table 5: Slump results with untreated UEO compared to TUEO

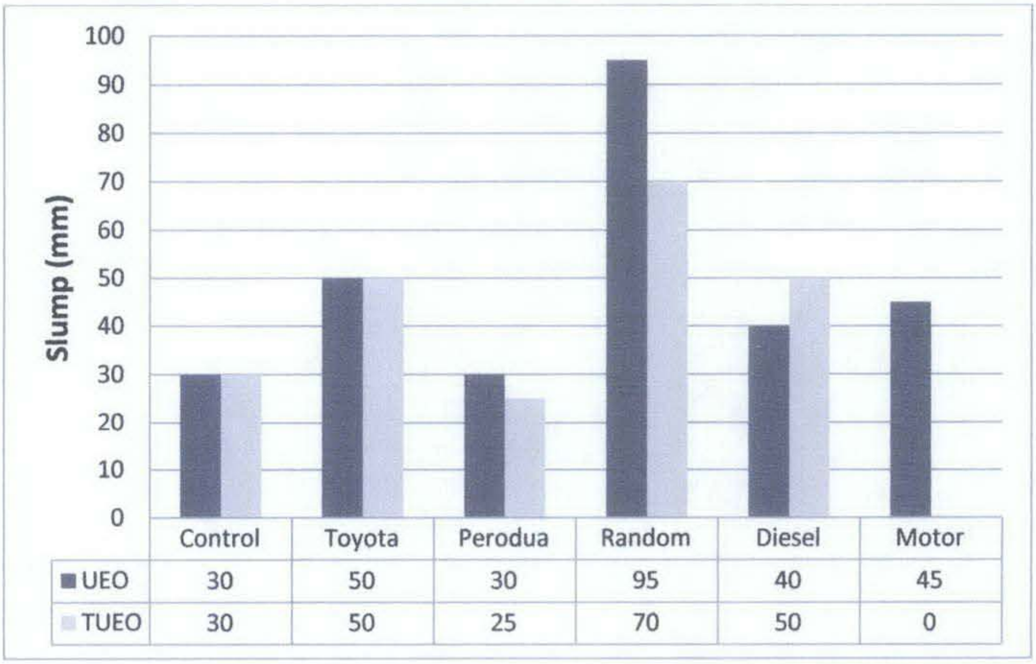


Figure 19: Slump achieved by each concrete mixes.

4.3.2 Compressive strength test results

28-day compressive strength of concrete cubes all 10 concrete mixes are shown in Table 5 and Figure 18. It is noticed that all concrete mixes with UEO and TUEO as admixture show lowered compressive strength compared to the control mix. This may be due to increased in porosity that is occupied by oil.

Admixture	Compressive Strength (MPa)	pH of Admixture	Concrete Slump (mm)
Control (No admixture)	41.01	-	30
Toyota UEO	39.04	7.12	50
Perodua UEO	30.29	6.53	30
Random UEO	33.5	6.01	95
Diesel UEO	39.9	7.28	40
Motor UEO	40.68	7.07	45
Toyota TUEO	38.94	7.24	50
Perodua TUEO	19.65	5.55	25
Random TUEO	26.39	4.5	70
Diesel TUEO	39.46	7.16	50

Table 6: Compressive strength of each concrete mixes, compared to pH of each admixture, and slump of each mixes.

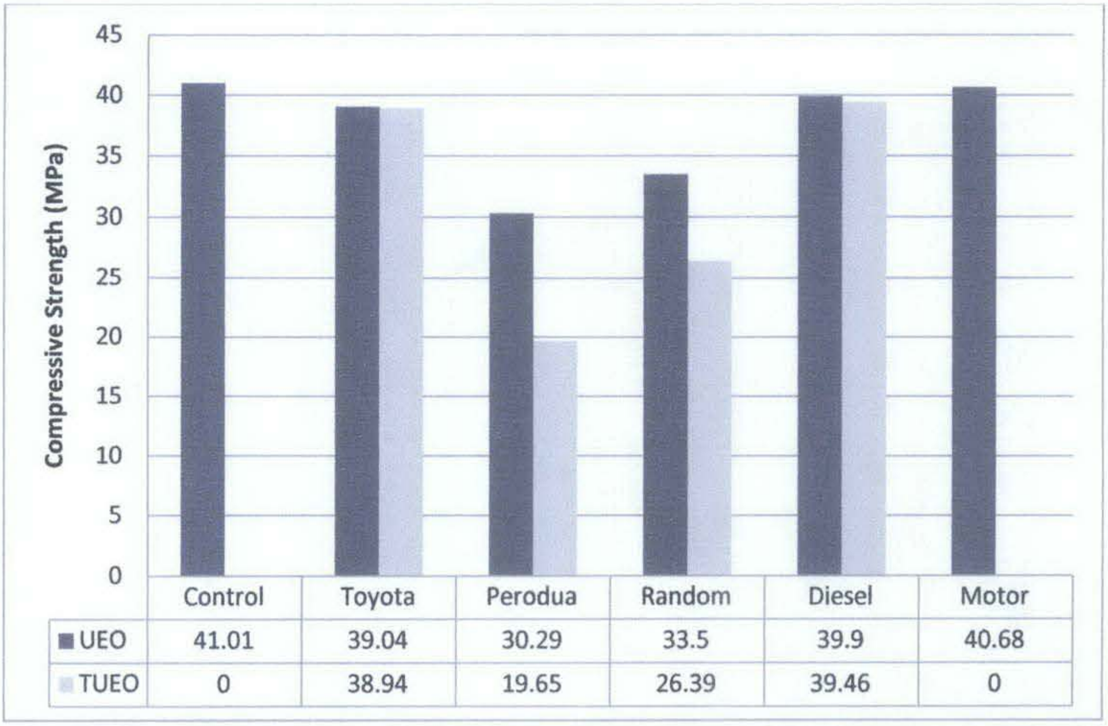


Figure 20: Compressive strength of all concrete mixes, with UEO concrete compared to their TUEO counterparts.

However a trend is noticed in the compressive strength data. Concrete cubes with low pH or acidic admixtures (UEO or TUEO) all show decrease in compressive strength when compared to concrete cubes with admixture that is not acidic, which have pH values above 7 (refer to Figure 19). For example, Random UEO that has pH value of 6 produced cubes with 33.5 MPa in strength, while the Random TUEO that has pH value of 4.5 produced cubes with 26.39 MPa in strength. This has confirmed with the literature that acids can have deleterious effects on concrete strength, which in this case is an internal acid attack. Concrete with admixture with pH of 4.5 have a strength reduction of almost 40% when compared to the Control Mix that has no admixture.

Acids in the admixture reacted with the cement components, which are mainly alkaline compounds such as $Ca(OH)_2$, CaO, C_3S,C_2S, C_3A and C_4AF. Reaction of this acid attack will result in formation of salts that are non-cementitious. In the case of sulphuric acid attacks, $CaSO_4$ salts are formed, while phosphoric acid attacks produce $CaPO_4$. The loss of calcium in the cement grains in the acid attacks can cause low C-S-H hydration degree during the concrete hardening process, thus reducing the strength of the concrete.

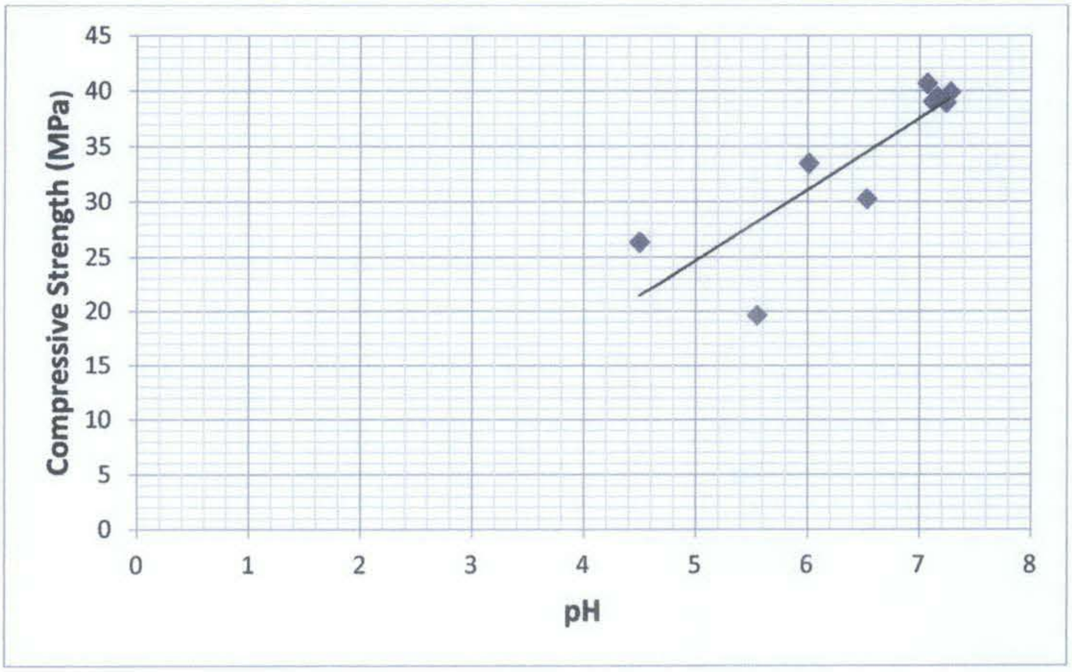


Figure 21: Compressive strength vs. pH of admixture.

Slump also affects the compressive strength of the concrete cubes. It is noticed that concrete with admixture that gives higher slump have higher compressive strength, maintaining the strength to the level of the Control mix. However it is not necessary that UEO as admixture can improve the concrete slump. Low slump is achieved when Perodua UEO and TUEO were used as admixture, with 30mm and 25mm respectively. Combining with the acidity of Perodua UEO and TUEO, it is noticed that the compressive strengths are significantly reduced, by 25% and 50% respectively.

Fresh concrete with low slump have poor workability, where cement and aggregates tend form agglomerates. These agglomerates can lead to low w/c regions, which limits cement hydration in those areas, while allowing other regions to be higher than nominal w/c, thus subsequently leading to reduced strength in the hardened concrete. Honeycombs were also form due to low workability, which contributed to reduced strength.

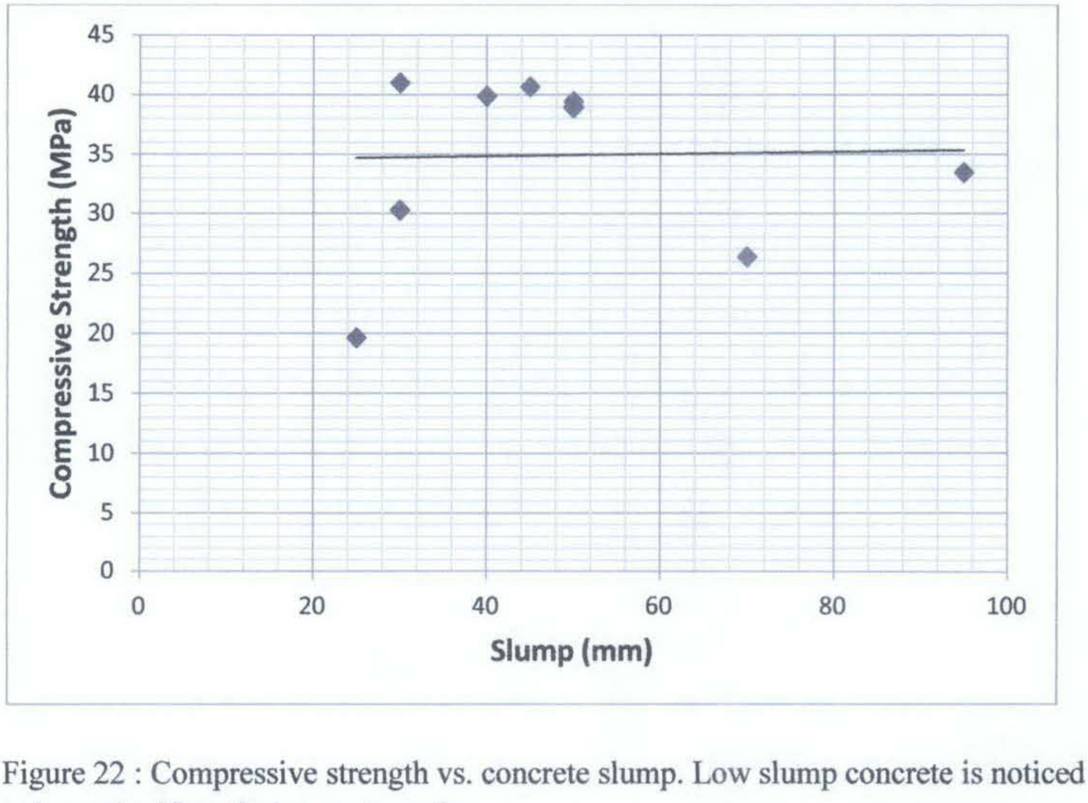


Figure 22 : Compressive strength vs. concrete slump. Low slump concrete is noticed to have significantly lower strength.

4.3.3 Porosity tests results

Porosity of all the concrete mixes was found to be in the range of 10.5%-12.2%. It is noticed that all concrete with UEO or TUEO as admixture shows slightly higher porosity than the control mix, except Perodua UEO and TUEO. This could be due to the oil that remained in the hardened concrete during curing process and is later leached away, leaving behind pores that previously occupied.

There are not much difference between porosity of UEO and TUEO, however it is noticed that increase in porosity in TUEO Perodua and TUEO Random compared to their UEO counterpart. The increase in porosity is in conjunction with the decreased compressive strength of the TUEO Perodua and TUEO Random, when compared to their UEO counterparts.

This shows that the decrease in strength can also be attributed from the increase of porosity in the concrete. However this proves that UEO can improve air-entraining in concrete, thus improving some durability against freeze-thaw. Calculations of concrete porosity for this project are shown in Appendix II.

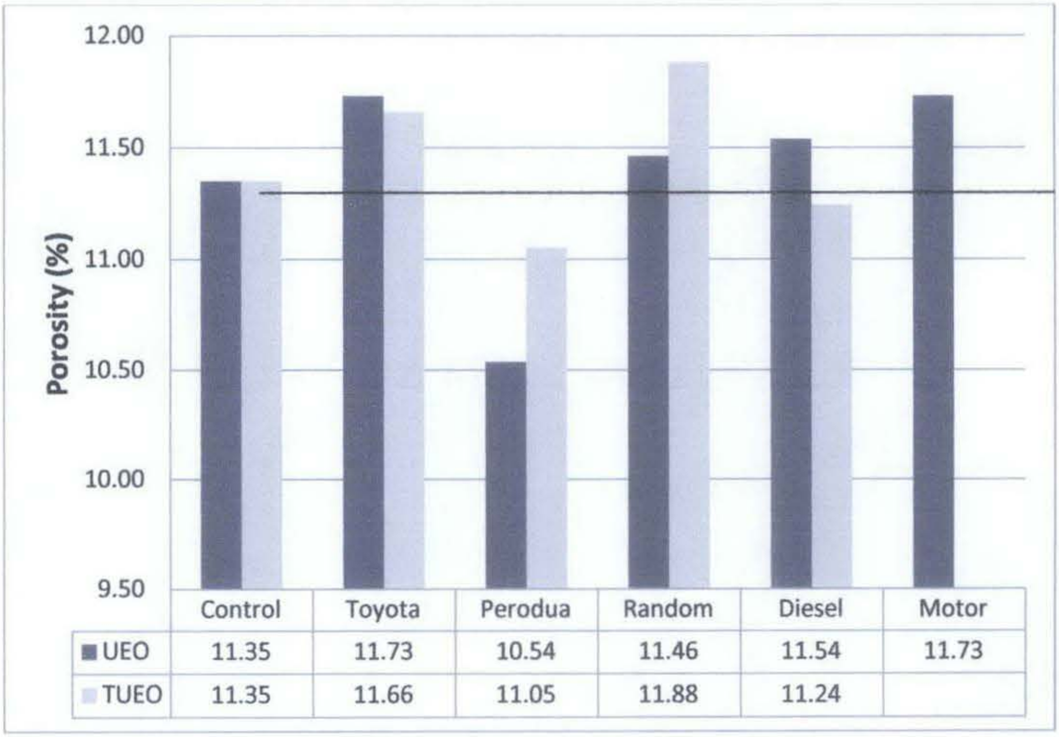


Figure 23: Porosity of UEO mixes compared to TUEO mixes.

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The main research objectives of this project is to treat used engine oil (UEO) into a more benign UEO for concrete using ionic liquid (IL), as well as to determine the effects of varying types of UEO with varying chemical impurities on concrete.

In conclusion,

1. Small scale testing of treating UEO have been carried out by using 5 different types of IL : 2-hydroxy ethylammonium formate (HEF), bis(2-hydroxylethyl) methyl ammonium formate (BHEF), 2-hydroxyethyl ammonium acetate (HEA), 1-n-butyl-3-methylimidazolium thiocyanate ([bmim][SCN]), and 1-butyl-3-methylimidazolium acetate ([bmim][Ac]).
2. Test shows the potential of treatment of UEO using ionic liquids, where good phase separations were achieved between certain UEO with certain IL, especially HEF, BHEF, and BmimSCN. However, not all UEO can be successfully separated. Simple observation shows that HEF gives better phase separation from the five UEO samples than its HEA and BHEF counterparts. BmimAc has failed to be separated from the Diesel sample even after addition of water. This may be due to the high amount of aromatics in the Diesel sample, which will dissolve into immidazolium ionic liquids which have aromatic cations. On the other hand, BmimSCN gives very good separation from Perodua sample.
3. Observations on the levels of UEO phase and IL phase, as well as density test have also shown some of the hydrocarbon may have dissolved into the ionic liquids and vice versa, due to cross-solubility.
4. Only HEF was used for producing treated UEO (TUEO) for concrete testing in this project. Unfortunately, even though impurities removal rates by HEF were good, Perodua TUEO and Random TUEO produced by HEF were increased in acidity due to unknown chemical reaction, causing the concrete strength to decrease significantly. It is unknown that why Toyota UEO and Diesel UEO treated by HEF did not have increase in acidity. Thus, more research is needed on HEF effects on different types of UEO.
5. Different types of UEO can give different concrete slump. However it is noticed that concrete with UEO and TUEO of the same type gives similar concrete

slumps with little differences. This may indicate that the super-plasticizing and dispersing effects given by UEO are more dependent on UEO physical properties instead of chemical properties.

6. More significantly, this research confirmed the existence of acids in UEO. It is noted that admixture (UEO or TUEO) with high acidity can severely decrease the compressive strength of the concrete, where admixture with pH of 4.5 can reduce the compressive strength up to 40% when compared to control mix.
7. This experiment have also confirmed with previous research done on UEO, where UEO or TUEO that is not acidic can increase the slump of concrete while maintaining the compressive strength.
8. Porosity test on the concrete shows concretes with most UEO and TUEO have slightly higher porosity than control mix, which may be the reason why their compressive strength are also slightly lower. However this proves that UEO can improve air-entraining in concrete, thus improving some durability against freeze-thaw.

5.2 Recommendations for future works

Due to time constraint of this project, there are plenty of aspects in this topic that are yet to be look into.

1. To better understand the effects of individual impurities compounds of UEO on concrete fresh and hardened properties, variables such as acidity, type of base oil, have to be controlled by using a standard UEO produced by certified chemical standard makers. This standard UEO should have fixed, known chemical and physical properties, as well as known concentration of impurities found in regular UEO. With a standard UEO as reference, XRF quantitative analysis can be made by calibrating the XRF machine with this reference. Since the concentration of chemical compounds in the standard UEO are known, these concentrations can also be manipulated for various tests.
2. It is well known that used ionic liquids can be recovered, regenerated and be reused. A follow up research on regenerating used ionic liquids of this project can be conducted in enhancing the sustainability of such technology, as well as to save cost.
3. It was noticed that acidity of UEO can significantly affect concrete strength, thus a novel and easy way of treating UEO may be achieved by neutralizing these acids with alkaline solutions such as calcium hydroxide or sodium hydroxide.

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Appendix I

Concrete Mixing Volume Calculations:

For each mixes, fresh concrete samples are used for slump test and air entrainment test. Three 10x10x10cm concrete cubes samples are made for 28th day compressive strength test. Porosity test sample is comprised of one 15x25x5cm slab, which will then be cored into a 5cm diameter cylinder. The following shows the total volume of concrete mix to be made for each mixes:

Volume for air entrainment test	0.008m^3
Total volume of 3 cubes	0.1m×0.1m×0.1m×3= 0.003 m^3
Volume of slab for porosity test	0.15m×0.25m×0.05m= 0.001875 m^3
Total Volume of samples	0.012875 m^3
Total volume with errors (+30% of total)	0.0167375 m^3

Due to limited amount of ionic liquid, 0.016 m^3 or 16 litres of concrete mix are made to minimize the usage of ionic liquid. The following table shows the weight of each ingredient used for each mixes:

Cement (kg)	325 kg/ m^3×0.016 m^3= 5.2kg
Water (kg)	0.55×325 kg/ m^3×0.016 m^3= 2.86kg
UEO (kg)	0.005×325 kg/ m^3×0.016 m^3= 0.026kg
Fine Aggregate (kg)	757.3 kg/ m^3×0.016 m^3= 12.1168 kg
Coarse Aggregate (kg)	1137.5 kg/ m^3×0.016 m^3= 18.2 kg

Appendix II

Calculations for concrete porosity

	Weight in Air, Wa(g)	Weight in Water, Ww(g)	Displaced water (g)	Oven-dried Weight, Wd (g)	pore water (g)	SG of concrete	Porosity (%)
Control	254.1	151.9	102.2	242.5	11.6	2.373	11.35
Toyota	266.3	157.2	109.1	253.5	12.8	2.324	11.73
Perodua	271.9	159.9	112	260.1	11.8	2.322	10.54
Random	266	155.2	110.8	253.3	12.7	2.286	11.46
Diesel	275.8	161.4	114.4	262.6	13.2	2.295	11.54
Motor	261.4	154	107.4	248.8	12.6	2.313	11.73
Control	254.1	151.9	102.2	242.5	11.6	2.373	11.35
Treated Toyota	258.5	149.6	108.9	245.8	12.7	2.242	11.66
Treated Perodua	272.2	160	112.2	259.8	12.4	2.316	11.05
Treated Random	276.2	159.2	117	262.3	13.9	2.242	11.88
Treated Diesel	261	152.5	108.5	248.8	12.2	2.293	11.24

$$Porosity = \left(\frac{Wa - Wd}{Wa - Ww}\right) \times 100\%$$

Appendix III

Tools used in project

Activities	Tools
Ionic Liquid Testing and Treatment of UEO	- 25ml bottles, vials, beakers - magnetic stirrers, - pipette
Concrete Mixing	- Concrete mixer - Poker vibrator - 10cm mould - Plywood and 2x1 inch timber - Hand tools: Hammer, trowel, tamping rod
Concrete test	- Slump cone - Measuring tape - Vacuum saturation pump - Coring machine

Appendix IV

Gantt chart of FYP over two semesters

Week Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Literature review & research	▨	▨	▨	▨	▨	▨	▨																					
Collection of samples							▨	▨	▨																			
Chemical analysis of UEO										▨	▨	▨	▨								▨	▨	▨	▨				
Ionic liquid testing										▨	▨	▨	▨	▨	▨	▨	▨											
Chemical extraction of UEO for concrete tests																	▨	▨	▨	▨								
Concrete Mixing and Slump Test																			▨	▨	▨							
Compressive Strength and Porosity Test																							▨	▨	▨	▨		