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Nottingham**

**School of Bioscience, Agricultural and
Environmental Science Division**

Utilization and disposal of drilling mud waste in Libya

By

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Declaration

The work described in this thesis was conducted at the University of Nottingham, School of Bioscience, Agricultural and Environmental Science Division during the period between Oct.2014 to Nov. 2019. I declare that this work is my own and not submitted for a degree in another university.

Dedication

This Ph.D. thesis is dedicated to my beloved Parents, my sincere wife, and my trigger in this life my sons Ahmed, Ashraf and daughters Aya and Arwa

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Abstract

The production of oil and gas includes drilling a number of wells for exploration or production activities. During drilling operations, large volumes of drilling fluids are used to facilitate the process. In Libya, after completion of drilling operations drill cuttings and waste drilling fluids are typically discharged close to the oil fields without treatment. This can result in negative ecological impacts on the surrounding environment e.g. through infiltration of toxic constituents into soils and underground waters.

In recent years, the use of sustainable technologies to remediate drilling waste has attracted greater attention and is a good choice for Libya where infrastructure and resources limit the feasibility of using conventional treatment strategies. Among the sustainable approaches available, soil stabilisation techniques e.g. solidification/stabilisation (S/S) of contaminated soil using conventional or innovative binders, and stabilisation of contaminated soil through phytoremediation using plants and grasses are promising options.

In this work these two approaches were examined to test their suitability for use in Libyan Desert. The solidification/ stabilisation of drilling waste via geopolymerisation approach was tested using industrial by-products such as brick and steel industry by-products or using natural kaolin clay. The ability of the geopolymers to stabilise drilling waste by immobilising heavy metals and encapsulating hydrocarbons was evaluated through systematic experiments employing both macro properties and microstructure studies to assess: (i) the transformation of raw materials into cementitious materials; (ii) changes in physical and mechanical properties, (iii) the role of additives in enhancing the degree of geopolymerisation (iv) the leachability of solidified waste- geopolymers produced, and (v) the effect of aging for one year in Libyan Desert climate on the durability properties for produced (S/S) systems.

The research has resulted in a number of key conclusions related to the feasibility of using Kaolin based geopolymers to stabilise the drilling waste generated from oil and gas industry in Libya.

It is found that (S/S) systems composed from kaolin-waste geopolymer able to reduce the contaminants leachability by both physical (adsorption or encapsulation) and chemical (fixation) means, and it is possible to use Kaolin as a sustainable alternative for Portland cement in S/S system to convert the hazardous waste into inert or

nonreactive hazardous waste acceptable for selected in-situ environmental engineering applications. The solidified geopolymer matrix found adequate to the requirements of sustainable waste management options such as safe landfill, reuse and recycle in the place of the generation which offering a sustainable, cost-effective approach that brings environmental and economic benefits.

Phytoremediation of drilling waste contaminated soils was tested using a native Bermuda grass species. A glasshouse experiment evaluated the ability of grass to survive, uptake and/ or stabilisation of HMs and degradation of TPHs in contaminated soils. In this study, Bermuda grass was planted in soil comprising different ratios of soil: waste to examine the effect of a range of HMs and TPHs concentrations. Biomass measurements including shoot biomass, grass height, leaf area, roots height and density were made, in addition to testing for any reduction in leachability of HMs and TPHs contamination, and the role of microorganisms and enzymes in the dissipation of petroleum hydrocarbons.

This research suggested that Bermuda grass is a useful species for phytoremediation of soils contaminated by drilling waste, and has the capability to stabilise the HMs in the roots and rhizosphere soils. Bermuda grass also is shown to have the potential to remediate soils contaminated by petroleum hydrocarbons when the contamination level below 7350 mg kg⁻¹ TOC. The grass offers an environmentally-friendly, cost-effective waste management option for some sites despite requiring a longer time. Results from this study are helpful for further field phytoremediation studies.

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List of Abbreviations

ρ	Density of water =1 g.cm ⁻³ .
α	Degree of geopolymerisation reaction
A	mass of oven dried sample in air (g)
AMR	Average metabolic response
AWCD	Average well colour development
B	mass of surface dry sample after immersion (g)
BR	Brick industry remains
BS	British Standard
C	Mass of surface dry sample after immersion in boiling water (g)
C10-C16	Carbon atoms number in Fraction 2
C16-C34	Carbon atoms number in Fraction 3
CAH	Calcium aluminate hydrate
CASH	Calcium aluminum silicate hydrate gel
CFA	Calcium ferrite hydrate
CH	Calcium hydroxide
CMD	Community metabolic diversity
CSH	Calcium silicate hydrate
D	Apparent mass of the sample in water after immersion and boiling water (g)
DHA	Dehydrogenase activity
EC	Electrical conductivity
EPA	U.S. Environmental Protection Agency
ETS	Electron transport system
FA	Fly ash
FTIR	Fourier transform infra-red
g1	Bulk density, dry (mg.m ⁻³)
g2	Apparent density (mg.m ⁻³)
GC-FID	Gas Chromatography -Flame ionization detector
GC-MS	Gas Chromatography- mass spectra
GN2	Gram-negative Biolog plates
HDPE	High density Polyethylene
HM	Heavy metals
IC	Ion chromatography
ICP-MS	Inductive coupled plasma -Mass spectrometry
IS	Iron slag
K	Natural kaolin clay
L	Path length

M	Alkali cation ion (Na^+ or K^+),
MK	Meta-Kaolin (calcined kaolin clay)
MPa	Mega Pascal
M_{plant}	Elemental concentrations of each metal in the plant
M_{soil}	Elemental concentrations of each metal in the plant
n	The degree of geopolymerisation
NAFs	Non-aqueous fluids
NPK	Sodium-Phosphorus- nitrogen fertilizer
NSAH	Sodium silicate aluminate hydrate
OBM	Oil based Mud waste
OC	Organic Carbon
OD	Optical density
OPC	Ordinary Portland Cement
PAHs	Polycyclic aromatic hydrocarbons
pH	Buffering capacity
RPM	revolutions per minute
S/S	Solidification/Stabilisation
SI	Steel industry waste
T	Time taken for pulse to travel along the sample (μs).
TC	Total Carbon
TCE	Trichloroethylene
TCLP	Toxicity characteristic leaching procedure
TF	Triphenyl formazan
TOC	Total Organic Carbon
TPH	Total petroleum Hydrocarbons
TTC	Triphenyltetrazolium chloride Dye
UCT	Unconfined Compression Test
UPV	Ultrasonic Pulse Velocity
V	Pulse velocity (km/s)
w	The amount of bound water
W1	Sample original weight
W2	Unreacted material weight
WBDFs	Water-based systems
WBM	Water Based Mud waste
XRD	X-ray diffraction
XRF	X-ray fluorescence
V_{plant}	Elemental concentrations of Vanadium metal in the plant

V_{soil}	Elemental concentrations of Vanadium metal in the soil
z	Si:Al molar ratio

Chapter 1: Introduction and literature review

1. Introduction: Background to the thesis and problem formulation

Libya is considered as one of the most important producers of oil and gas in Africa and the world. The Libyan economy depends substantially on this sector with 96.7% of exports related to the oil and gas industry (WTO, 2015; World Economic Forum. (2019). The National Oil Cooperation (NOC) in Libya promotes an increase in crude oil and gas production to provide financial resources for the development of this sector and the Libyan economy in general.

This development includes drilling of wells for exploration and production. During drilling operations, large volumes of drilling fluids/muds used to facilitate the drilling process and are critical to ensuring a safe and productive well (IPIECA/OGP, 2014). After completion of drilling operations, drill cuttings along with waste drilling muds are usually discharged close to the oil field without treatment and have the potential to cause significant negative ecological impacts on the surrounding environment through infiltration of toxic constituents into soil profiles and groundwater (Figure 1.1). This problem in Libya is resulting in substantial environmental impacts and the task of cleaning up this waste is an important issue for the country (Biltayib, 2006).



Figure 1.1. Waste disposal during drilling operations in Libya

1.1 Generation, composition and toxicity of drilling waste

During drilling operations, thousands of tons of heterogeneous wastes are generated. The majority of this waste is drill cuttings and spent drilling fluids. Drill cuttings are particles of crushed rock produced by the action of the rotary drill bit as it penetrates into the earth. Drilling fluids facilitate the drilling process by transporting cuttings to the surface, preventing well-control issues, improving wellbore stability, minimizing formation damage, cooling and lubricating the drill string. They are pumped through closed loops from mud tanks on the rig, down the drill pipe, exiting through holes in the drill bit, and are returned to the surface via the annulus, which is the space between the drill pipe and the drill casing or rock wall of the drilled hole. As the drilling fluid exits the drill bit, it suspends cuttings and carries them up the annulus to the surface where they are separated from the drilling fluid by the solids control equipment on the drill rig (IPIECA. 2014). The drilling fluid is recycled, stored or transferred to landfill or for treatment.

1.1.1 Drilling Fluids Types and Composition

Drilling fluids are mixtures of fine-grained solids, inorganic salts, and organic compounds dissolved or dispersed/suspended in a 'continuous phase' (the base fluid) which may be water or an organic liquid continuous phase.

1.1.1.1 Water-based systems (freshwater and saltwater systems) WBDFs

Water-based drilling fluids (WBDFs) are the most widely used and are generally less hazardous. Figure 1.2 illustrates the general composition of the liquid phase and chemical content of WBMFs by weight.

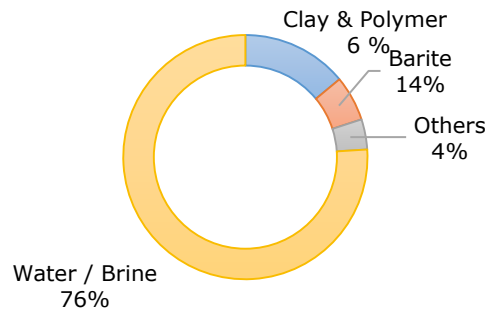


Figure 1.2. Composition (weight %) of typical WBDFs (IOGP 2016).

They are formulated mixtures of clays, natural and/or synthetic organic polymers, mineral weighting agents, and other additives dissolved or suspended in fresh water, seawater or brine. Different formulation of WBMFs may be required to meet the technical physiochemical properties required in each section of the well.

1.1.1.2 Non-aqueous fluids NAFs

Non-aqueous fluids (NAFs) can be classified based on their aromatic hydrocarbon content into three groups. Group I comprise high-aromatic content fluids that include crude oil, diesel and conventional mineral oils. These fluids are refined from crude oil and contain levels of total aromatic between 5-35 wt. %. Group II are medium-aromatic content fluids and contains products produced from crude oil with levels of total aromatic between 0.5 and 5 wt. %, often known as 'low toxicity mineral oil'. Group III are fluids with low/negligible-aromatic content fluids and includes highly refined mineral oils with levels of total aromatics below 0.5 wt. % and polycyclic aromatic hydrocarbon (PAH) levels below 0.001 wt. %, according to the OGP definition (OGP 2016). Collectively these three groups of muds, also known as Oil-Base Drilling Fluid Systems, are used when a high degree of inhibition and thermal stability is needed during drilling operations. Figure 1.3 shows typical proportions of the liquid phase and chemical content of non-aqueous fluid types as a percentage by weight NAFs.

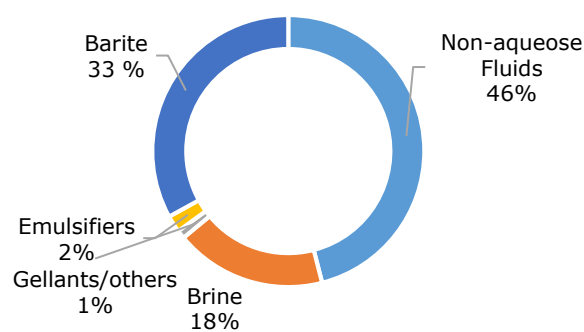


Figure 1.3. Composition (weight %) of typical NADFs (IOGP 2016).

1.1.1.3 Common additives

Number of chemical products used as additives in both WBDFS and NAFs to adjust their physical and chemical properties and enable optimal function during the drilling process.

Table 1.1 lists common additive categories with examples.

Table 1.1: Common additives to WBMFs and NAFs (IOGP 2016).

Category	Examples
Weighting materials	Barite, calcium carbonate, ilmenite or hematite
Viscosifiers	Clay, organic polymers
Filtrate reducers	Starch, clay, lignite, polymers
pH control	Inorganic acids and bases, most often caustic soda
Shale control	Soluble salts such as potassium chloride (KCl), amines, glycols)
Lost circulation materials	Inert insoluble solids such as calcium carbonate, groundnut shells, graphite, mica and cellulose fibres
Lubricants	Water-based lubricants, glycols and beads
Emulsifiers	Surfactants detergents, soaps, organic fatty acids
Thinners	Lignite, lignosulfonates, polymers
Flocculants	Inorganic salts, acrylamide polymers
Bactericides	Glutaraldehyde, triazine disinfectants
Pipe-freeing	Agents Water-based lubricants, enzymes, surfactants
Defoamers	Alcohols, silicones, Aluminium stearate, alkyl phosphates
Calcium reducers	Sodium carbonate, bicarbonate, polyphosphates
Corrosion inhibitors	Amines, phosphates
Temperature stability	acrylic or sulfonated polymers, lignite, lignosulfonate

1.1.2 Toxicity of Drilling Waste

Drilling wastes are the second largest volume of waste generated by the oil and gas industry after produced water (Onwukwe and Nwakaudu, 2011). The main pollutants in spent muds are biocides, oil, completion or stimulation fluid components, corrosion inhibitors, reservoir fluids (crude oil, brine), and drilling mud chemical components. Its disposal is considered one of the most complex environmental problems facing the oil and gas exploration and production industry (Agwa et al., 2012). Table 1.2 lists the environmentally significant constituents of drilling wastes, their impact depends primarily on the material and its concentration after release (Onwukwe et al., 2012). Waste drilling muds are believed to be toxic and should be regulated (ERMS, 2006).

Table 1.2: Waste components and environmentally significant constituents resulting from drilling activities (Onwuka et al., 2018).

Type of Waste	Main Component	Possible Environmentally impacts
Waste Lubricants Spacers	Lube oil, greases Mineral oil, detergents, surfactants	significant constituent Heavy metals and organics
Spent/contaminated water-based muds (including brine) Water-based mud cuttings	Whole mud, mineral oil, biodegradable matters	Hydrocarbon, alcohol, aromatics
Spent/contaminated oil Based muds	Formation solids, water- based muds, mineral oil	Heavy metals, inorganic salts, biocides, hydrocarbons, solid cuttings, BOD, organics
Oil Based Mud cuttings	Whole mud mineral oil	Heavy metals, inorganic salts, biocides, hydrocarbons, solid cuttings
Spent Bulk Chemicals	Formation solids, oil- based muds, mineral oil	Heavy metals, inorganic salts, hydrocarbons, solid cuttings, BOD, organic, surfactants
Spent special products	Cement, bentonite, barites, viscosities, thinners, fluid loss reducers, specialty product	Heavy metals, inorganic salts, hydrocarbons, solid cuttings
	H2S scavengers, defamers, tracers	Heavy metals hydrocarbons, organic, solids

1.1.3 Waste Management in Libya

In Libya many challenges prevent execution of waste management solutions for drilling waste produced from oil and gas drilling operations. The main problems are the lack of appropriate infrastructure and technical experience needed for management and disposal for this type of waste (Ehmiada, 2008). Previously drilling waste was temporarily stored in earthen pits close to drilling operations before disposal to land or permanent burial in the pits. This management option provides a simple and low-cost approach but is an unsuitable solution for wastes containing high concentrations of oil, salt, toxic metals or other harmful components that could migrate and contaminate potable water resources. As drilling operations, increase accumulation of drilling waste is becoming a more prominent and worsening issue for the country and the need for a simple solution is highly desirable.

Several environmental impacts of the Libyan upstream petroleum industry have occurred and accumulated overtime since petroleum exploration and production began (Ehmiada, 2008). These impacts are various, including gas emissions due to the high temperature during whole the year in the desert region, land contamination, groundwater pollution which have a detrimental effect on the soil quality and plant growth close or away from the place of drilling waste generation due to the high soluble salts, heavy metals, and petroleum residue contents in drilling waste. This resulting contamination of ground and surface water can lead to serious impacts on local people, animals and vegetation.

1.2 Drilling waste management options

Much research is currently being directed towards providing sustainable solutions to minimize the environmental impact of drilling operations (Knez et al., 2006). A wide range of techniques and technologies are under consideration, but no single option is appropriate in all cases. A combination of different management options is typical for

particular project, and dependent on factors including fluid type, location, proximity to existing facilities, regulatory requirements, availability of suitable end-uses and financial considerations (IOGP 2016).

1.2.1 Biological Treatment Technologies

Bioremediation technologies can be broadly classified as ex-situ and in-situ. Ex situ, technologies involve the physical removal of the contaminated material in the treatment process. In contrast, in situ techniques involve treatment of contaminated material at the place of generation e.g. using microorganism promoted enzymatic degradation or transformation of contaminants to less toxic or nontoxic forms (Boopathy, 2000). This approach is extensively used, and increasingly effective, for the treatment of hydrocarbons. Microorganisms have the capacity to degrade the majority of natural hydrocarbon components, especially saturated and unsaturated alkanes, monoaromatic and low-molecular-weight polycyclic aromatic hydrocarbons (PAHs) (Brzeszcz and Kaszycki, 2018). High-molecular weight PAHs, resins and asphaltenes are more resistant to biodegradation (Ward et al., 2003). Yao et al. (2012) observed that microorganisms could affect the migration and transformation of heavy metals through changing their physical and chemical characteristics. Mechanisms include complexation, precipitation, oxidation-reduction reaction and extracellular & intracellular accumulation. The main factors effecting the success of biodegradation process are difficulties in adjusting environmental conditions such as nutrients, temperature and pH of the media (Conner, 1990).

Land farming (also known as spreading, land disposal and land treatment) is a bioremediation technology used to treat hydrocarbon-contaminated soils (Ayari et al., 2010). It is considered the simplest bioremediation techniques due to its low cost and the fact that is less reliant on specialist equipment. Contaminated soils are mixed with soil amendments, and then the mixture is incorporated into the soil and periodically cultivated for aeration. Contaminants are degraded, transformed, and immobilized by

microbiological processes and oxidation. Many studies confirm that the land farming is an economically viable bioremediation technique for soils contaminated with crude oil, its derivatives such as gasoline, kerosene and diesel (Mmom et al., 2010; Cetin et al., 2014) or PAHs (Silva-Castro et al., 2011; Mizwar et al., 2016). Conversely, other studies suggest it is ineffective for the treatment of soils contaminated by heavy metals (Khan et al., 2004) or for remediation of soils contaminated by chlorinated hydrocarbons such as trichloroethylene (TCE) due to its low solubility, toxicity to microorganisms and conversion to more toxic vinyl chloride as a result of biodegradation (Cai et al., 2012). Although simplicity and cost-effectiveness are the major advantages of land farm approaches, the treatment has physical, chemical and biological 'constraints' which must be addressed.

Phytoremediation is an innovative and attractive alternative to conventional remediation methods because the treatment can be done *in-situ* using plants. The cost of this technique is lower than the most other technologies and it is relatively 'environmentally' safe. In this approach plants compete with microorganisms for nutrients, including (carbon, hydrogen, oxygen, micro and macro nutrients) and use the light as a source of energy to transform organic compounds to CO₂ and H₂O and use inorganic nutrients drawn from the environment to synthesize amino acids and vitamins needed for plant growth. Growing plants has the potential to decrease the bioavailability of soil contaminants such as heavy metals and organic compounds (Newman et al., 2009; Tang et al., 2010; Razzaq R, 2017). The degradation of organic contaminants can be achieved through mechanisms that include plant-promoted microbial degradation, plant uptake and accumulation, Phytovolatilisation, Phytodegradation or Rhizodegradation (Ansari, 2016).

1.2.2 Physical and Chemical Processes

Physical and chemical approaches include thermal, slurry injection, stabilization and solidification/stabilization techniques. Recycling using physical and chemical techniques and re-use of waste materials is also an option.

Thermal techniques involve the use of high temperatures for waste incineration (500-1500°C) or waste desorption (400-1500°C), suitable for the removal of hydrocarbon wastes. The technique requires advanced additional treatment units for the combustion gases and aerosols produced (Vidonish et al., 2016). The main disadvantage of thermal approaches is the high cost, the difficulty of moving large volumes of waste and the inefficiency for treating heavy, toxic and radioactive elements which remain after combustion and require further advanced treatment (Huang et al., 2018).

Slurry injection involves processing of solid particles of cutting waste into small pieces and then mixing them with fluid (water, seawater, fresh water, used drilling muds, or produced water) to make a slurry. The slurry is injected underground into a suitable confined formation using high pressures. A permanent disposal of drilling wastes can be achieved using this type of treatment. However, the underground geology and the existence and depth of underground water must be investigated before utilization of this technology. There are several technical problems that can occur during implementation of slurry injection including operational issues that cause the injection process to slow or stop, and environmental problems e.g. leakage of injected fluid to the ground surface or the seabed (Dusseault, 2005).

Stabilization is the process of immobilizing waste materials in a confining medium. In this technique chemicals are added to contaminated soil to change the waste into a safe form which is not easily absorbed by the soil or plants (Kinigoma, 2010). Ideally, this *in-situ* fixation or stabilization does not interrupt the environment or generate hazardous wastes. The general approach for stabilization processes involves mixing treatment agents (binders) to contaminated soil. Inorganic binders include clays (e.g.

bentonite or kaolinite) (Garau et al., 2007; Sheta et al., 2003; Wuana and Okieimen, 2011), cement (Chen et al., 2009; Kogbara et al., 2013), pozzolanic materials e.g. fly ash (Asiabadi et al., 2014) or blast furnace slag (Goodarzi and Salimi, 2015), calcium carbonate (Bade and Sik, 2012), Fe/Mn metals or oxides (Arshadi et al., 2014), charcoal, activated carbon (Zietzschmann et al., 2014), zeolite (Hunce et al., 2012), organic stabilizers such as bitumen (Iwański and Chomicz-Kowalska, 2013), composts, manures (Song et al., 2014) or a combination of organic-inorganic amendments.

Solidification/stabilization systems involves mixing of waste (e.g. drilling mud) with a stabilizing solidifying agent (typically cement) followed by a hydration step which is best suited for inorganic wastes such as heavy metals and radioactive waste. Cement is frequently the stabilizing solidifying agent of choice. Cement-based S/S aims to immobilize contaminants by converting them into less soluble forms (stabilization) and encapsulating them by the creation of a durable matrix (solidification). Portland cement, thermoplastic materials (e.g. bitumen, sulfur polymers) and lime are collectively termed 'primary stabilizing agents', whilst ground granulated blast furnace slag, pulverized fuel ash, and natural pozzolanic materials which possess cementitious properties are termed 'secondary binders' (EPA Guide Report, 2001).

In recent years, as a result of the trend to reduce pollution from cement manufacturing operations, much research has been conducted on the use of geopolymer as alternatives to cement in attempts to reduce the global warming resulted from production of cement (Heath et al., 2014). Geopolymers are alkali-activated aluminosilicate binders that have high compressive strength, low shrinkage and acid resistance properties (El-Eswed et al., 2015). Solidification/Stabilization of heavy metals using geopolymers has received considerable attention (Zhang et al., 2015). Geopolymer matrices provided a satisfactory binder for the immobilization of heavy metals because of their low permeability and durability (Van Jaarsveld et al., 1999). Leachability of contaminants

from stabilized geopolymer wastes is generally lower than that of hardened Portland cement stabilized wastes (Shi et al.,2011).

Many of the materials in the drilling waste stream can be re-used or recycled more than once or be converted into a usable material (Mostavi, Asadi and Ugochukwu, 2015: Blash et al., 2017). Table 1.3 illustrates different potential use of drilling waste.

Table 1.3: Typical drilling waste management strategies (Onwukwe et al., 2012)

Waste Minimization	Recycle or Re-use	Disposal
Synthetic and oil-based muds generate fewer cuttings than water-based muds	Road spreading when roads benefit from application of waste	Land spreading/ farming
Coiled tubing drilling	Re-use synthetic and oil-based muds	Road spreading
Directional /horizontal drilling	Use cleaned cuttings for fill or cover materials	Burial in on-site pit or off-site landfill
Use of less toxic components and additives for muds	Restoration of wetlands with clean cuttings	Discharge to ocean
Air Drilling	Use cuttings as an aggregate for concrete or bricks	Salt cavern disposal

A range technique, often in combination have been used for the treatment of petroleum hydrocarbon contaminated soil. Each method has advantages and disadvantages and selection of appropriate techniques depends on the individual waste properties and factors including sustainability, cost, time and availability of infrastructure.

Table 1.4 highlights selected current advances in the treatment of drill cuttings and compares the technologies in terms of cost, time and space requirements. The table provides a current comparison of Thermal, physical, chemical and bioremediation technologies and for the treatment of contaminated drill cuttings providing information on a number of factors that need to be considered when choosing the best technology for drilling waste management including the environmental risks associated with disposal of drilling wastes.

Ball et al., 2012 reported that cost is the most important factor that need to be considered when choosing the best technology for drilling waste management; other factors include the local environment, safety aspects and the relevant regulatory framework.

Table 1.4: Comparison between treatment options for drilling waste (Ball et al., 2012).

Treatment	Space Requiremen	Time for treatme nt	Cost (GBP)	Monitoring required	Physical requirements	Capital requirements	Advantages	Disadvantages
Composting/ biopiling	Land area required (10 m ³ t ⁻¹)	56–8 days	30-42	Regular pollutant, temperature and moisture monitoring	Impermeable or plastic lined base. Wood or straw, water and manure required	General lifting and windrow turning equipment. Vessel if closed composting	Rapid, complete removal of pollutants. Production of useful by-productcompost	Volatile hydrocarbons may be released into environment. Fire risk.
Land farming	Large area of soil required (1 ha per 20 t)	200-800 days	5-7	Regular monitoring of pollutant concentration in soil and runoff	Field with good soil microbial activity. Manure, and water may be added	Spreading equipment	Complete removal of pollutants. Low cost	Slow process-pollutants may build up on repeated applications
Land treatmen	Very large area required (1 ha per 6 t)	400–1200 days	2-3	Regular monitoring of pollutants	Large areas of soil with good drainage.	Spreading equipment	Complete removal of pollutants. Very low cost	Very slow processrequires long-term monitoring
Phytoremidation <i>Bioaugmented landfarming</i>	Significant land required	100-200 days	8-12	Regular monitoring of pollutants	Field with good soil microbial activity. Manure, nutrients and water may be added	Spreading equipment. N, P and K needs to be added	More rapid removal of pollutants than land-farming alone	Requires nutrients and regular monitoring
Burial pit	Use of existing reserve pit only	500–3000 days	5-7	Regular monitoring for pollutants in ground water	May need to blend drill cuttings with soil	Some earth-moving equipment	No transportation costs. On site treatment	Long term monitoring required. Finite area. Anaerobic conditions reduce biodegradation rate
Landfills	Large area with clay or lined base	200-2500 days	20-32	Long-term monitoring of site required	Large area away from inhabitants with clay or lined base	Transportation of drill cuttings to	Burial so cuttings are buried. Relatively	Long-term monitoring and site restoration. Many legislative

Chemical solidification/stabilization	Very low space requirement	1–2 ton / h	50-125	Long-term monitoring of stabilized product	Range of chemicals required for solidification/stabilization	landfill site-excavation equipment required Significant costs for equipment to enable solidification	low cost Low space, rapid treatment	issues. Slow biodegrading rates Large set up costs. Risk associated with long term stabilization
Incineration	Small, portable equipment	5-6 ton / h	250-550	Temperature and flue gas monitoring	1200–1500°C	2.6–3.65 million GBP required in set up costs	Waste reduction. Low retention times. Complete removal of pollutants	Large costs associated with setting up and running incineration
Thermal desorption	Small, sometimes mobile equipment	3–10 ton / h average	200-750	Temperature and flue gas monitoring	220–500°C	0.26–4.2 million GBP required in set up costs (depending on size)	Waste reduction. Portable equipment. Low retention times	High equipment and running costs. May not remove all pollutants

As illustrated in table 1.4, the conventional techniques used for treatment of drilling waste have many advantages and disadvantages. The classical management options utilized currently in Libya such as Burial or landfill of the waste in a pit close to the drilling operation sites offers low cost solution but needs very long time for treatment and required long term monitoring. Using of thermal management options expensive and environmental non-

From the several waste management approaches, S/S and phytoremediation techniques are perhaps the most suitable for developing countries due to their low-inputs and low-cost. Further work is required to specifically assess the efficiency of these approaches for the remediation of drilling waste in the context of the Libyan environment. Both approaches will therefore be considered in detail with a view to assessing their suitability for use in remediation of drilling waste generated during oil and gas industry activities in Libya.

1.2.2.1 Solidification/Stabilisation (S/S) of industrial waste

Solidification/stabilisation techniques use physical and /or chemical different fixation mechanisms to transform drilling waste to less hazardous forms. The process is accomplished by mixing waste with a solidification agent or binder. The binder forms a monolithic solid matrix by chemically reacting with the waste and either forms microscopic cells that encapsulate the waste, or coats and binds the individual particles together (Al-Ansary and Al-Tabbaa, 2007). The main aims of S/S in the context of drilling waste are to:

- convert the waste to a chemically stable form through sorption, precipitation or encapsulation into crystal lattices
- reduce the surface area of the waste to create a product that is resistant to leaching and has low mobility of environmental contaminants

- transform the waste into a useful final product e.g. a construction/building material.

To achieve these aims, binders used in S/S treatment should have the following advantages (Paria and Yuet, 2007):

- Physical and chemical long-term stability
- Good mechanical properties (strength and impact resistance)
- Non-toxicity of the chemical ingredients used in the S/S process
- High resistance to biodegradation
- Relatively low water permeability
- Relatively low cost and ease of use and processing

The most commonly utilised binders are Ordinary Portland Cement (OPC) and hydrated lime (Stegemann and Buenfeld, 2003). Solidification of waste using cement and lime is widely understood and simple (Malviya and Chaudhary, 2006). Both binders have an extensive and well documented history of use for the stabilisation of toxic elements including As, Pb, Cd and Hg (Palfy and Molnar, 1999; Vandecasteele et al., 2002; Yu et al., 2005). Both binders have a similar hardening hydration reaction mechanism. During the solidification process, concrete formation binds and strengthens the material, coats and incorporates the contaminant waste particles into siliceous crystal lattices, and block pathways between pores. The high alkalinity of both binders reduces the solubility and mobility of many inorganic toxic or hazardous metals (Camenzuli et al., 2013). Portland cement is most commonly used due to its relatively low cost and wide availability compared to lime (Kundu and Gupta., 2008).

1.2.2.1.1 Limitations of classical binders

The performance of solidified materials where classical binders has been used can be affected by the nature of the waste (Paria and Yuet, 2007). Classical binders also have considerable environmental considerations that should be considered before selecting any binder for (S/S) treatments (Bates and Hills,2015).

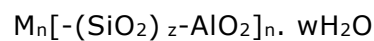
Water based wastes are most amendable by solidification/stabilisation using OPC and/or lime. Wastes which contain organic materials such as oil, organic solvents or dissolved polymers can interfere with S/S causing undesirable consequences (Arafat et al., 1999; Botta et al., 2004; Karamalidis et al., 2007). Organic materials retard the setting process by forming a protective layer around the binder or waste grains, hindering the hydration reaction and the formation of calcium hydroxide required for setting (Paria et al., 2007). Organic compounds are lipophilic and do not combine tightly with CaO, resulting in a low fixation ratio in S/S of organic contaminated soil (Yu et al., 2016). Breakdown of the solidified matrix affects the compressive strength of the final product and in some cases forms amorphous structures after drying (Ghasemi et al., 2017).

Production of both cement and lime releases greenhouse gases directly and indirectly: heating of limestone releases CO₂ directly, whilst burning of fossil fuels to heat the kiln indirectly results in CO₂ emissions. The cement industry is one of the largest producers of carbon dioxide CO₂, it generated around 2.8bn tonnes of CO₂, equivalent to 8% of the global emissions (Carbon Brief, 2019). Lime production is typically the second largest industrial process responsible for CO₂ emission in most of manufacturing countries after cement production (Shan et al., 2016).

The present rate of release of this greenhouse gas into the atmosphere is a serious threat to future life and prosperity on the planet. Thus, most industrialized countries have introduced legislation and incentives in order to regulate and reduce the activities of the sectors most responsible for greenhouse gas emissions (Imbabi et al., 2012). At the same time research is encouraged to find ways in which to reduce the consumption of cement and lime in S/S using different approaches (Noor-ul-Amin, 2012) or alternative binders such as aluminosilicate materials (Krishnan, 2014; Zhang et al., 2014).

1.2.2.1.2 Geopolymers as alternatives to classical binders in S/S

The term “geopolymer” was first used in the 1970s by *Prof.* Joseph Davidovits and is used to define alkali-activated cement or inorganic polymer concrete. Geopolymers are aluminosilicate networks formed as result of the reaction between silicate-rich and aluminate materials with a highly alkaline activation solution (Davidovits, 2002). Several minerals and industrial by-product materials that contain unreacted amorphous silica (SiO_2) and alumina (Al_2O_3) have been investigated as primary precursors for the production of geopolymers. Calcined industry by-product materials (e.g. iron slag or fly ash) or calcined clay (metakaolin) have been proven to produce geopolymers with a higher compressive strength and homogeneous microstructure than OPC (Pereira et al., 2018). The most common alkaline liquid used to initiate geopolymerisation is concentrated sodium hydroxide NaOH or potassium hydroxide KOH, or a mixture of MOH solution with water glass i.e. Na_2SiO_3 or K_2SiO_3 (Zejak et al., 2013). Barbosa et al., (2000) proposed that the final chemical formula of a geopolymer is:



Where **z** is the Si/Al molar ratio, **M** the alkali cation (Na^+ or K^+), **n** the degree of polymerisation and **w** the amount of bound water. The reaction between the raw materials and the alkali activator is a polymerization reaction in contrast to OPC that undergoes hydration to form a cement paste. In geopolymerisation, the starting material (fly ash, iron slag, metakaolin or kaolin) mixed with the alkali activator solution results in a reaction which produces a disordered alkali aluminosilicate gel. The activator solution provides alkali ions and hydroxyl ions. Once sufficient dissolution has occurred an aluminosilicate network begins to form a gel that hardens. Gelation, reorganisation, polymerisation and hardening reactions occur simultaneously and once the reaction is complete the water is released or goes into the pore structure of the gel (Sindhunata et al., 2006).

Geopolymers have emerged as novel engineering materials for construction applications primarily due to their lower environmental footprint (Roy, 1999; Van Deventer et al., 2012; Srinivasan et al., 2013; Heath et al., 2014). Their low cost, availability of raw materials and their unique physical, chemical and mechanical properties are also important (Arioz et al., 2012). Many recent studies (e.g. Duxson et al., 2007; Obonyo et al., 2011; Habert et al., 2016) have shown that there is potential to use geopolymers in environmentally sustainable applications. They have unique properties including high early strength, low alkali-aggregate expansion, resistance to freeze-thaw cycles and high resistance to chemicals like sulfates, chlorides and dilute acids (Bakharev et al., 2003; Abdollahnejad et al., 2014).

A number of studies have confirmed acceptable performance of geopolymers in different waste management applications including immobilization of toxic and heavy metals and radioactive wastes (Perera et al., 2004; Li et al., 2013). A large and growing body of literature has focussed on the performance of geopolymers for the immobilisation of heavy metals and radioactive waste using (i) Metakaolin based geopolymers (Cheng et al., 2012; Brown et al., 2013; Renew et al. 2016; Zhang 2016), (ii) fly ash based geopolymers (Dermatas et al., 2003; Zhang et al., 2013; Ariffin et al., 2017) and (iii) iron slag geopolymers (Yunsheng et al., 2007; Abdel-Gawwad et al., 2016; Mahendran et al., 2016). These studies clearly demonstrate that the produced geopolymer-waste system effectively immobilised heavy metals and exhibited high mechanical strength. Also, it has been reported that geopolymers are highly suitable for radioactive waste immobilization due to an amorphous three-dimensional structure which results in high thermal stability, resistance to aggressive environments, low leachability and low cost (Kuenzel et al., 2015; Li et al., 2013).

Longhi et al., (2019) reported that the reaction mechanism through which geopolymers 'set' is not fully understood, however polymerization occurs rapidly compared to hydration reactions in cement that are typically mostly complete within one month but

not fully completed for up to a year. It has been suggested that the immobilisation of heavy metals within geopolymers may be via: (i) ionic reaction or ion exchange with sodium (Na^+) or other alkali ions (K^+ , Mg^{2+} and Ca^{2+}) (Cheng et al., 2012), (ii) adsorption of heavy metals into the amorphous geopolymer gel structure (Bin Guo et al., 2017), or (iii) precipitation of metal hydroxides due to the neutralisation effect and the physical encapsulation of heavy metal precipitates within the geopolymer network structure (Cheng et al., 2012).

Little investigation has considered to use of geopolymers for the remediation of soils contaminated with hydrocarbons. The presence of hydrocarbons affects the S/S strength using classical binders (OPC and lime) resulting S/S product has a poor compressive strength (Karamalidis and Voudrias, 2007), therefore, it is necessary to add pozzolan and/ or adsorbent materials which can absorb hydrocarbon constituting within the cement blocking or use binders that increase sorption of organic compounds and undergo different drying mechanisms to prevent the detrimental effects on binder hydration (Leonard and Stegemann, 2010).

1.2.2.1.3 Geopolymer Formulation and Mechanical Performance

Several variables affect the alkaline activation of the aluminosilicate materials, most prominently the composition and physical properties of the raw materials used (particle size, chemical composition, phase content, silica and reactive alumina content); type and concentration of the alkaline activator; liquid/solid ratio; curing temperature and time; and moisture conditions during initial curing (Luukkonen et al., 2018; Wang et al., 2019). These variables affect the degree of reaction, the mineralogical composition and microstructure of the reaction products and ultimately the physical-mechanical properties of the material (Zivica et al., 2015).

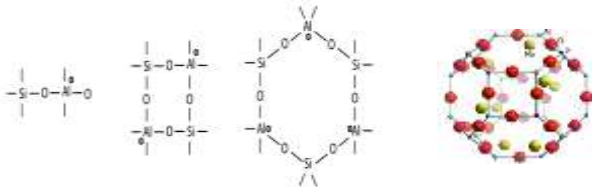
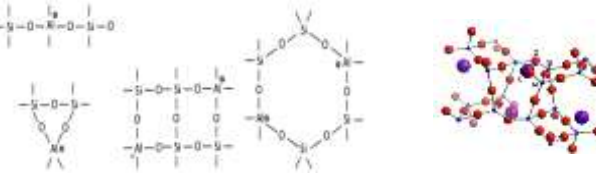
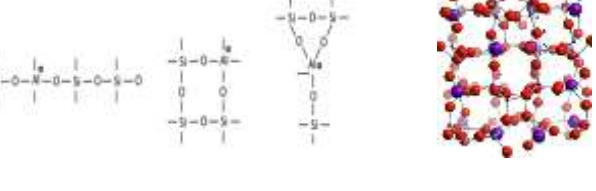
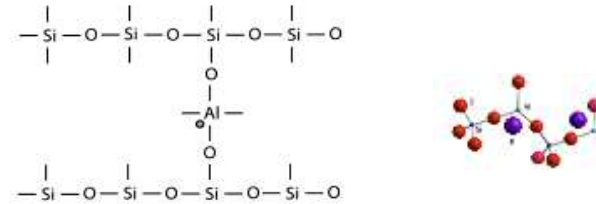
The main source of aluminates and silicates in geopolymer systems are the raw materials (precursors) and added materials such as waste. Some materials are rich in

SiO₂ (e.g. fly ash, slag, and rice husk) whilst others are rich in Al (e.g. clays including kaolin, and metakaolin). Much of the current literature suggests that the SiO₂:Al₂O₃ ratio has a significant effect on the microstructure and porosity of geopolymers factors that influence the strength and performance of the final product. (Duxson et al., 2007; Saidi et al., 2013).

During the geopolymerisation reaction, a strongly alkaline solution initiates the reaction by dissolving silicates and aluminates and convert them to tetrahedral SiO₄ and AlO₄ (Sani et al., 2016). In later reaction steps, these tetrahedral units are linked through shared oxygen atoms to form three different types of geopolymer products as shown in Table 1.5 (Abdullah et al., 2011). The shape of the framework formed significantly affects the microstructure, porosity, strength characteristics and general behaviour of the geopolymer. Davidovits, 2011; Joshi et al., 2012 found that longer chains of 3d framework result in more flexible, elastic or ductile behaviour in the geopolymer product, whereas shorter and smaller 3d frameworks result in denser packing, and subsequently stronger reaction towards compressive loads.

Studies conducted on metakaolin geopolymers suggested an optimum molar ratio of SiO₂:Al₂O₃ in the range of 3.0-3.8 gave better physical, mechanical properties and leachability behaviour attributed to the formation of a homogenous microstructure in the geopolymer (Aly et al., 2008). Moreover, metakaolin geopolymers produced using SiO₂:Al₂O₃ molar ratio over than 4 had a very porous matrix, which resulted in low compressive strength (Kuenzel et al., 2016).

Table 1.5: Geopolymer products classified according to their $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio (Davidovits 2008; Zhuang et al., 2016; Djobo et al., 2016).

$\text{SiO}_2:\text{Al}_2\text{O}_3$	Geopolymer type	Structure
2	PS type Poly-sialate [$-\text{SiO}_4-\text{AlO}_4-$]	
4	PSS type Poly-sialate-siloxo [$-\text{SiO}_4-\text{AlO}_4-\text{SiO}_4-$]	
6	PSDS type Polysialate-disiloxo [$-\text{SiO}_4-\text{AlO}_4-\text{SiO}_4-\text{SiO}_4-$]	
>6	Sialate link	

For environmental applications, the lower $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio results in larger surface area of geopolymer, which is beneficial for improving desorption capacity and the efficiency in immobilization of toxic and heavy metals and encapsulation of compounds (Duxon et al., 2005; Zheng et al., 2009). Exceeding a ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ of 3.8 (Based on reactive silica quantity) results in the development of micro-cracking which substantially weakens the materials and reduce the mechanical strength (Rowles et al., 2009). Addition of sodium silicate Na_2SiO_3 as source of reactive silica enhances formation of the alumni-silicate gel and consequently results in a higher mechanical strength in the final material (Wang et al., 2012).

Molar ratios of other key components e.g. Na_2O , K_2O and H_2O used in geopolymers are influence the final mechanical properties. Published studies have also described the influence of the ratios $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}:\text{Na}_2\text{O}$ on the microstructure and mechanical

properties of kaolin and metakaolin geopolymers (Kamalloo et al., 2010). Optimum molar ratios to achieve the highest compressive strength in the final geopolymer are:

3.0-3.8 for $\text{SiO}_2:\text{Al}_2\text{O}_3$, 1-1.2 for $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ and 10-12 for $\text{H}_2\text{O}:\text{Na}_2\text{O}$.

Common alkaline activators are NaOH, KOH and waterglass ($\text{Na}_{20} \cdot n\text{SiO}_2$). Sodium hydroxide and sodium silicate solutions are most commonly used because they are widely available and result in good mechanical properties (Phoo-ngernkham et al., 2016). It has experimentally proven that compressive strength, apparent density and the content of the amorphous phase of metakaolin based geopolymers increases with increasing NaOH concentration within the range 4–12 M (Chi, 2015).

Phair and Van Deventer, (2001) found that increasing concentration of alkali activator increases pH and enhances dissolution and production of smaller chain oligomers and monomeric silicate and soluble aluminum. Increasing pH also increases the solubility of aluminium which aids reaction with available calcium present in the raw material to produce calcium aluminum silicate hydrate gel (CASH) cement phases.

Water content also influences geopolymer formation as it takes part in all dissolution, hydrolysis and polycondensation reactions steps. It provides the medium for the dissolution of aluminosilicates, transfer of ions, hydrolysis of Al^{3+} and Si^{4+} compounds and polycondensation of different aluminate- and silicate-hydroxyl species. During curing and drying of the geopolymer water is expelled from the matrix. In a similar way to OPC systems, mechanical properties (setting time, strength and microstructure characteristic such as permeability and leachability behavior) were negatively affected by increasing water to solid ratios in geopolymer systems. The minimum water to cement ratio is ~ 0.4 by weight of OPC whereas geopolymers are readily workable at lower ratios (0.2-0.4) as reported by Liwa et al., (2011).

Curing temperature and time influence the geopolymerization reaction and final microstructure, porosity and mechanical properties (Khale and Chaudhary, 2007); Rovnaník, 2010; Mo et al., 2014). Elevation of curing temperature accelerates the dissolution of raw materials and the geopolymerisation reaction of precursors but has a negative effect on physical properties because rapid setting restrains development of a compact and tough structure. At ambient temperature, the geopolymerization reaction is extremely slow with slower early strength development and setting time as reported by Patel and Shah, (2018).

Efflorescence has a negative effect on the mechanical properties of geopolymers as reported by Zhang et al., (2014). Efflorescence is defined as the formation of a white layer on the outer surface of alkali activated geopolymers, this layer is typically composed of carbonate and bicarbonate salts of alkali and alkaline earth cations (Na, K, Ca and Mg). Geopolymers, particularly those produced using sodium hydroxide as the alkali activator, with a high $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ molar ratio can suffer from efflorescence problems caused by excess unreacted Na_2O . It is also partly due to weak binding or exchangeability of Na within the geopolymer structure (Sani et al., 2016). Sodium cations are mobile within the pore network, particularly when there is movement of moisture within the sample (Zhang et al., 2016) and temperature and humidity influence the content of water (H_2O) in the efflorescent salt (hydrous alkali carbonate).

Several studies suggest solutions to reduce efflorescence. Chemically, by the use of KOH instead of NaOH as been suggested by Skvara et al., (2008) because K is more strongly bound to the aluminosilicate gel framework (Duxson et al., 2006), and also because potassium carbonate crystals are usually less visually evident than sodium carbonates and bicarbonates. Utilizing different Al-rich mineral admixtures (ground granulated blast furnace slag, metakaolin, and several different calcium aluminate cements) to enhance microstructural density has also been suggested (Kani et al., 2012). Application of hydrothermal curing to increase the extent of reaction of the

natural aluminosilicate materials is an alternative suggested approach (Luukkonen et al., 2018).

1.2.3 Phytoremediation

Phytoremediation is a broad term that has been used since 1991 to describe the use of plants to reduce the volume, mobility, or toxicity of contaminants in soil, groundwater, or other contaminated media (USEPA, 2000). It is defined as a biological technology that uses living green plants for *in-situ* removal, degradation, or clean-up of pollutants including metals, pesticides, explosives, and oils. It is especially useful for low levels of soil contamination and can be used effectively in large areas (Ndimele, 2010). The plants also help to stabilise the area (**Phytostabilisation**). A considerable literature reports the ability of many plant species to grow in contaminated soils and detoxify pollutants present in the growth media by different mechanisms (Okunowo and Ogunkanmi, 2010). Some plants accumulate the toxic materials (metals and compounds) in their tissues (phytoextraction), others transform pollutants to less toxic compounds (rhizodegradation) or remove them from through phytovolatilization or filtration (rhizofiltration) (Table 1.6).

Table 1.6: Mechanisms in phytoremediation process (Dhir et al., 2009)

Process	Description	Media	Contaminants	Plants
Rhizodegradation Phytodegradation	Microbial degradation in the rhizosphere stimulated by plants	Soil, sludges, sediments	Aromatic & aliphatic petroleum hydrocarbons, chlorinated solvents, TNT, pesticides	Grasses, alfalfa, Hybrid poplar, <i>Brassica</i> , <i>Typha</i> , <i>Jatropha</i> , <i>Cassia</i> , <i>Bermuda</i>
Phytostabilization	Stabilization of contaminants by binding/complexation	Soil, sludges, sediments	Metals (As, Cd, Cr, Cu, Pb, Zn)	Sunflower, <i>Chenopodium</i>
Phytoextraction	Uptake of contaminants into roots by accumulation or collection of harvestable shoots	Soil, sludges, sediments	Metal (Cr, Cu, Ni, Cd, Zn, Ag) and radionuclides	<i>Alyssum</i> , <i>Brassica</i> , <i>Thlapi</i> , sunflower
Phytovolatilization	Volatilization of contaminants from leaves	Soil, sediment	Se, Hg, As	<i>Poplar</i> , <i>Phragmites</i> , <i>Scirpus</i>

Phytoremediation efficiency relies on the ability of plants to take up and/or metabolize pollutants to less toxic substances (Koptsik, 2014; Bech et al., 2016). The uptake, accumulation and degradation of contaminants vary from plant to plant. The plants used in phytoremediation should not only accumulate, degrade or volatilize the contaminants, but should also grow quickly in a wide range of different conditions (Oh et al., 2014). Plants are therefore generally selected on the basis of their growth rate and biomass, their ability to tolerate and accumulate contaminants, the depth of their root zone, and their potential transpiration rate (Tangahu et al., 2011).

The successful application of plant species for bioremediation of oil- and heavy metals contaminated soil has been described in a number of studies (Basumatary et al., 2012; Asiabadi et al., 2014; Agnello et al., 2016). A recent review concluded that the removal of organic contaminants is accomplished by Rhizodegradation where contaminants are degraded in the rhizosphere (the area surrounding the roots of the plants) by microbial activity that is enhanced by addition of fertilizers (Maqbool et al., 2012; Asim Shahzad et al., 2015). The efficiency of rhizoremediation depends on the plant species used, its morphology (roots), physiology (root exudates), its adaptation for abiotic stress such as heat, cold, drought, salinity, nutrient availability and the concentration of pollutant present in the soil, and biotic stresses (stress that occurs as a result of damage done to an organism by other living organisms, such as bacteria, viruses, fungi, parasites living in rhizosphere region (Atkinson and Urwin, 2012). Several studies also concluded that the immobilization of heavy metals in phytoremediation of contaminated soils is achieved through phytostabilisation mechanism where the HMs absorbed in the root system or precipitated in the rhizosphere (Cristaldi et al., 2017; Razzaq, 2017).

The efficiency of different wild grass species including Bermuda grass for remediation of petroleum hydrocarbon contaminated soils has been evaluated in many studies (Sinha et al., 2007; Hussain et al., 2018). Bermuda grass (*Cynodon dactylon*) is a

potential candidate for rhizoremediation due to its highly branched root systems and toleration to the hot and/ or dry climate condition as reported by Razmjoo and Adavi, (2012). Saraeian et al., (2017) also, reported that Bermuda grass had a peculiar tolerance to petroleum hydrocarbons pollution and suggested that this species is typical and efficient species for phytoremediation petroleum-contaminated sites.

1.3 Conclusions

In considering, the literature related to the treatment and disposal of hydrocarbon contaminated drilling waste the following points emerge:

- Petroleum hydrocarbons and heavy metals are significant environmental contaminants in drilling waste, and their long-term persistence can pose a severe threat to the surrounding environment
- Disposal of contaminated drilling waste to landfill is costly and does not represent a sustainable solution as the pollutants may be mobilized by the action of rain or wind to the surrounding environment
- Despite the existence of efficient hydrocarbon treatment methods, traditional treatments, including thermal and slurry injection, are expensive due to the requirement for associated equipment and infrastructure. They are also considered to be time consuming and environmentally destructive techniques
- The sustainability of remedial approaches has attracted much greater attention in recent years, among these S/S and phytoremediation approaches are the most sustainable and particularly applicable to removal of contaminants from drilling waste where infrastructure and resources limit the feasibility of conventional remediation strategies
- Solidification/stabilization is considered as a simple and cost-effective treatment technology for hazardous waste contains heavy metals and radioactive materials.
- By utilising S/S technology, hazardous waste is transformed to a non-hazardous solid matrix that has acceptable physical and mechanical properties adequate to the requirements of sustainable treatment options such as safe landfill, reuse and recycle

- Little research has examined the efficiency of S/S treatment methods for the fixation of organic compounds
- Geopolymer technology has gained a great deal of interest for its potential applications in water, wastewater and solid waste treatment during the last decade. Geopolymers have good physical, chemical and mechanical properties, and considered as low-cost materials, which further enhances the environmental and economic feasibility.
- Bioremediation treatment methods appear to be an effective and potentially low-cost due to their lack of infrastructure requirements
- Bermudagrass is important warm-season cultivar, tolerant to Desert climate condition and considered as an efficient species for phytoremediation of petroleum-contaminated soil

1.4 Research purpose and thesis objectives

The purpose of this research was to study, identify, and propose simple and cost-effective solutions for the treatment of hazardous drilling waste. Two sustainable waste management options, S/S through geopolymerization and phytoremediation have been considered and examined for their efficiency and applicability in the desert climate of Libya. The specific objectives of the study were to:

- Investigate the applicability of S/S using industry by-product, low cost locally sources natural clay and additives to convert drilling waste into a solid geopolymer matrix with structural integrity compatible for in-situ storage, landfill, or re-use.
- Investigate the potential of Bermuda grass for phytoremediation of soil contaminated by drilling waste contain heavy metals and petroleum hydrocarbons

The principal objective of this research was to develop a practical scheme for the treatment of drilling waste using the mentioned technologies (S/S) and/or phytoremediation to reduce the risks associated with the generation of drilling waste in the Libyan desert. This required treatment or degradation of different types of drilling waste containing high concentrations of petroleum hydrocarbons and heavy metals, and reduction of the present discharge levels of residual petroleum hydrocarbons (more than 5000 mg kg⁻¹) to below regulatory (1,000 mg kg⁻¹) levels which provide the minimum risk to health, the environment, and ecology.

1.5 Thesis Organisation

This thesis consists of five main research chapters that address the following aspects: Characterizations of the raw materials and drilling waste samples used in this study and a review of the principle methods of materials testing to examine the efficiency of S/S treatment. and phytoremediation treatment approaches

- (i) Lab-scale experiment to evaluate the efficiency of using of industrial by-products such as steel industry waste (SI) or brick industry remains (BR) in S/S of drilling waste through geopolymerisation
- (ii) Lab-scale experiments to evaluate the use of natural kaolin clay and metakaolin in S/S of drilling waste through geopolymerisation
- (iii) Field experiments to investigate the effect of aging, durability and leachability behaviour of Kaolin-waste geopolymers and PC-waste systems
- (iv) Glasshouse phytoremediation experiments for clean-up of drilling waste using warm season grass (Bermuda grass)
- (v) A final chapter evaluates the experimental results and considers the applicability of the tested approaches for the treatment of drilling waste in Libya and recommendation for future studies.

Chapter 2: Materials and method

2.1 Introduction

The objective of this chapter was to characterize the raw materials and drilling waste used in this investigation and review the principle methods of materials testing. Standard and non-standard tests and procedures are described.

The chapter is sub-divided into several sections. First, the materials used in the work are described including, sampling procedures, physical and chemical characterization and toxicity classification. Second, the methodology used to investigate solidification/stabilization through geopolymerisation is described, including macro- and micro-structure studies to understand the relationship between chemical composition and geopolymer durability and environmental performance. Techniques for testing and analysis of materials including classical physical, chemical and mechanical testing techniques are also described. Third, the methodology followed to study the suitability of phytoremediation for cleaning up and/or stabilisation of drilling waste contaminated soils in desert climate is then outlined together with tests of the degradation of petroleum hydrocarbons in the rhizosphere. The biological tests used to quantify (i) microbial metabolic capabilities, (ii) the functional diversity of the microbial community in the contaminated soil, and (iii) enzymatic activity, which is used as an indicator of overall soil microbial activity.

To assess the effectiveness of (S/S) technique in the treatment of two different types of drilling waste, a systematic experimental study was taken through two approaches (macroscale and microstructure studies) as outlined in figure 2.1:

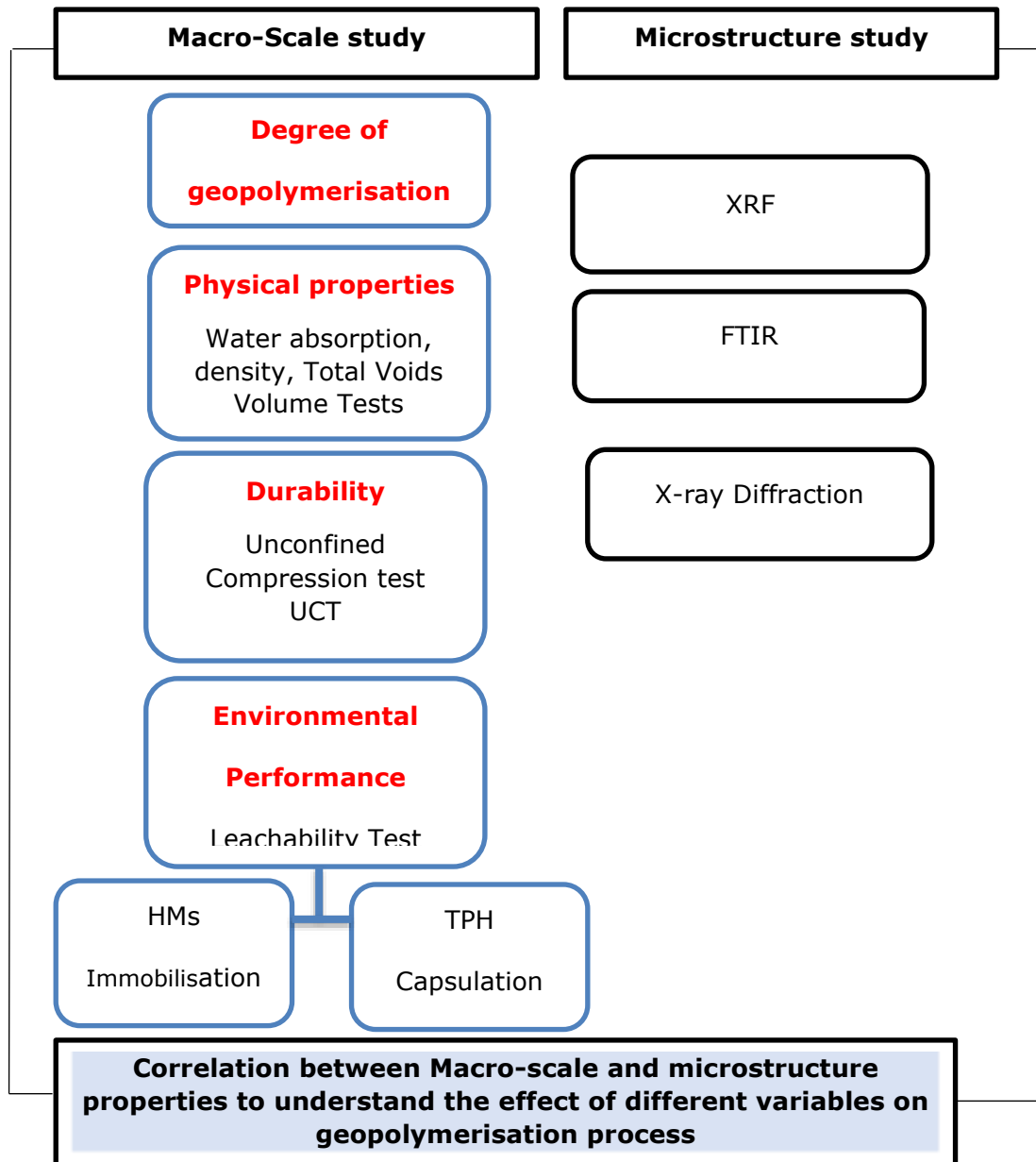


Figure 2.1. Solidification/Stabilisation experimental approaches

The macro-scale studies were conducted to examine the degree of transformation of raw materials (binders & waste) to cementitious materials and to assess the physical and mechanical properties of solid phases produced through geopolymerisation using aluminosilicate materials and alkali activators or hydration reactions using cement and water, and to assess its environmental performance in the immobilisation of toxic and heavy metals and encapsulation of petroleum hydrocarbons. The

microstructure study was performed to better understand the geopolymerisation reaction and the effect of the additives in enhancement of the degree of geopolymerisation and formation of aluminate-silicate network. The information obtained from XRD and FTIR analysis was used to study the morphology and phase transformation of geopolymer gels and the microstructure rearrangement of binder-waste systems after undergoing geopolymerisation or hydration reactions.

The results obtained from macro-scale and microstructure studies together were used to understand the relation between the chemical composition of geopolymer- drilling waste systems, microstructure changes and the durability behavior and its effect on environmental performance compared with PC-drilling waste solidified systems.

2.2 Materials

2.2.1 Soil and drilling waste samples

Uncontaminated soil was collected c.250 km away from drilling operations. Samples were air dried and sieved to < 2mm. Samples of drilling waste (Figure 2.1) were placed in plastic containers for transport before careful hominization, air drying and sieving (< 2mm).

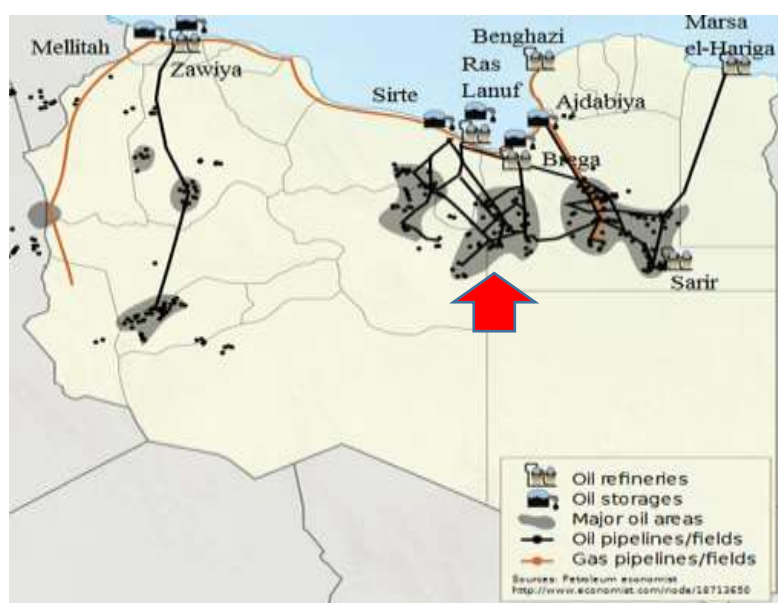


Figure 2.2. Locations where drilling waste was sampled

Water and oil-based drilling muds were sampled. Water-based mud (WBM) samples were collected from a waste pit (200 m long, 8 m width and approx. 1m depth) at location N (28056.696), E (022000.534) from different locations in the waste pit (Figure 2.2).



Figure 2.3. Water based mud sample collection and preservation

Oil-based mud samples were obtained from Jalu oil field (in the East of Libya) (Well No. 6J16-59E), N (28048.609), and E (021019.399) during drilling operations (Figure 2.3). The waste was collected from several locations in the waste pit (100 m long, 7 m width and approx. 1m depth).



Figure 2.4: Oil based mud sample collection and preservation

2.2.2 Binders

Conventional and non-conventional binders were obtained to test their efficiency in treatment of drilling waste samples. Portland cement type I (OPC) was obtained from

Alburg manufactory (Zliliten, Libya). It complies with the specifications defined by the ASTM C150 standard and the Libyan standard specifications 340/97. Waste brick material (BR) was sourced from the scrap yard of Zliten Brick factory. The brick fragments were ground using a ball mill until they were < 0.1 mm. Steel industry waste (SI) composed from mixture from different oxides and silicates was collected from Musrata Iron and Steel Complex- Libya.

Natural kaolin clay (K) was sampled from the Temenhint area close to drilling operations. Samples were excavated from the sides of natural slopes, air-dried, crushed and sieved (<1 mm). Meta-Kaolin (MK) was prepared by calcination at 700°C for a period of 2 h to produce thermally activated clay with a high alumina content according to the method proposed by Wang et al., (2011).

2.2.3 Additives

Aggregate was sourced from a limestone quarry in the Al-Wahat area close to the drilling operations. Aggregate particles were washed to remove any adherent clay, dried and sieved to obtain material between 2-4 mm in size. An alkaline activation solution was prepared from sodium hydroxide (NaOH) and sodium silicate Na_2SiO_3 (high purity Fisher UK) dissolved in deionised water. Commercial lime was obtained from the Libyan local market and used to study reduction in efflorescence and geopolymer strength improvement.

2.2.4 Physico-chemical characteristics of soils and drilling wastes

Salt and moisture content, pH and loss on ignition were measured using conventional testing methods according to British standards. Particle size distribution and specific surface area of samples was measured by laser granulometry after removal of organic materials using hydrogen peroxide solution (wet method), BS EN 15933:2012.

The major and minor mineral phases present in the materials was measured using X-ray diffraction (XRD). Fourier transform infra-red (FTIR) was used to examine the microstructure composition and transformation of raw materials and produced new phases and the remaining materials. The major oxides content was measured by X-ray fluorescence (XRF). Heavy metals (HM) content was measured by ICP-MS spectrometry following acid digestion and ion chromatography (IC) was used to determine anions present in leaching solutions. Total petroleum hydrocarbons (TPH) present in drilling mud samples were analysed using a carbon analyser and GC-MS was used to measure and detect the categories of petroleum hydrocarbons present i.e. kerosene (C12-C15) and diesel (C8-C21). The concentration of key radionuclides in drilling waste samples was measured by gamma spectrometry.

2.3 Methods

2.3.1 Degree of Reaction

A reaction degree test was used as a tool to assess the success of geopolymerization and the hydration reaction of Portland cement systems containing drilling waste. The acid attack technique developed by Fernández-Jiménez et al., (2006) was used to identify and quantify the degree of reaction by dissolving only reaction products (gels) where unreacted materials (Oxides) remain unaffected.

The reaction degree test was used in the course of this research for the following purposes:

- 1-Monitor and evaluate the formation of geopolymer gel.
- 2-Study the effect of alkali activator concentration on geopolymerisation degree.
- 3-Study the effect of TPH on geopolymerisation reaction.
- 4-Evaluate the effect of adding lime on geopolymerisation degree and reducing the efflorescence reaction.

The principle of this reaction is based on the fact that strong acid media will dissolve all gels formed during the hydration reaction of cement such as calcium silicate hydrate

(CSH), calcium aluminate hydrate (CAH) and calcium ferrite hydrate (CFA) or gels formed during alkali activation or geopolymerization reactions such as sodium silicate aluminate hydrate (NSAH) or calcium silicate aluminate hydrate (CSAH).

Known amounts of sample were subjected to chemical attack using hydrochloric acid (HCl 1:20) solution at room temperature for 3 hours to dissolve reaction products and leave unreacted materials including non-activated oxides (silicates and aluminates). Remnants of the acid attack were filtered through Whatman qualitative filter paper and washed several times using distilled water, collected in ceramic crucible and burned in a muffle furnace at 1000 °C for two hours. After initial cooling, the crucible was transferred to a desiccator to finish cooling to ambient temperature. The weight of dry unreacted material was measured and the degree of geopolymerization or hydration was calculated and expressed using:

$$\alpha = \frac{W_1 - W_2}{W_1} \cdot 100$$

Where α = Degree of reaction (%), W_1 = Sample original weight (g) and W_2 = unreacted material weight (g).

2.3.2 Water Absorption

Water absorption characteristics used to predict the durability of geopolymers and cement-based concretes. Water absorption is closely related with pore structure and can be used to predict permeability behaviour of geopolymer-waste or PC-waste mixtures. The information can be beneficial for evaluating the effect of water: solid ratio, adding of additives and the effectiveness of the curing regime on strength and mechanical properties. British standard testing method BS EN 772-11 was used to measure water absorption. Test specimens were oven dried at 105°C for 24 h in an oven. Specimens were then immersed in water for 24 h and the absorption evaluated by difference in weight:

$$\text{Absorption after immersion in cold water, \%} = \frac{(B - A)}{A} \times 100$$

$$\text{Absorption after immersion in boiling water, \%} = \frac{(C - A)}{A} \times 100$$

Where, A= mass of oven dried sample in air (g), B=mass of surface dry sample after immersion (g) and, C=mass of surface dry sample after immersion and boiling (g).

2.3.3 Bulk density

The mechanical and permeability properties of any concrete type material are highly influenced by its density. A denser concrete generally provides higher strength, fewer voids and lower porosity which is reflected in the leachability of the samples.

The bulk and apparent density of the geopolymers and cement samples was measured according to the British standard BS EN12390-7 on samples after 28 days of curing in a defined temperature cycle. Samples of known weight and size were immersed in cold water for 24 and dried in air. Bulk and apparent density were calculated from:

$$\text{Bulk density, dry, } g_1 = \left[\frac{A}{(C - D)} \right] \cdot \rho$$

$$\text{Bulk density after immersion} = \left[\frac{B}{(C - D)} \right] \cdot \rho$$

$$\text{Bulk density after immersion and boiling} = \left[\frac{C}{(C - D)} \right] \cdot \rho$$

$$\text{Apparent Density, } g_2 = \left[\frac{A}{(A - D)} \right] \cdot \rho$$

Where: -

A= mass of oven dried sample in air (g)

B=mass of surface dry sample after immersion (g)

C=mass of surface dry sample after immersion and boiling (g)

D=apparent mass of the sample after immersion and boiling (g)

g_1 = bulk density (mg m^{-3})

g_2 = apparent density (mg m^{-3})

ρ = density of water = 1 g cm^{-3} .

2.3.4 Total Void Volume

Total void (pore) volume (%) was determined by measuring the porosity accessible to water using the standard method ASTM C642. The method involves saturating the porous network of the sample with a liquid of known density (water), measuring the difference in weight in three states (M_{water} , M_{air} and M_{dry}), and then exposing the sample to boiling water for a period of time and repeating the measurements. The porosity accessible was calculated using:

$$\text{Volume of permeable pore space (voids), \%} = \frac{(g_2 - g_1)}{g_2} \times 100$$
$$\text{or } \frac{(C - A)}{(C - D)} \times 100$$

Where A= mass of oven dried sample (g), B=mass of surface dry sample after immersion (g), C=mass of surface dry sample after immersion in boiling water (g), D=apparent mass of the sample in water after immersion and boiling water (g), g_1 = bulk density, dry (mg m^{-3}), g_1 = apparent density (mg m^{-3}) and ρ = density of water = 1 g. cm^{-3} .

2.3.5 Ultra Sonic Pulse Velocity (UPV)

Ultrasonic pulse velocity (UPV) testing was used as a non-destructive way to assess the homogeneity, integrity and quality of samples during the curing period according to British standard BS EN 12504-4:2004. An Ultrasonic Pulse Velocity kit (PUNDIT Plus) was used to pass a pulse of 54 kHz through the sample. The ultrasonic pulses were produced by an acoustic transducer, held in direct contact with one surface and received by a similar transducer in contact with the other end of the sample. The pulse velocity is calculated:

$$V = \frac{L}{T}$$

Where V = pulse velocity, L = path length, T = time taken for pulse to travel along the sample .

The quality of the sample in terms of uniformity, existence or absence of internal defects, cracks and segregation can then be assessed using the guidelines given in Table 2.1.

Table 2.1: Qualitative classification of the quality of concrete on the bases of UPV (Whitehurst, 1966)

UPV (m/s)	>4500	3500-4500	3000-3500	2000-3000	<2000
Quality of concrete	Excellent	Good	Doubtful	Poor	Very poor

Higher velocities indicate high density, good quality and integrity of the sample, while slower velocities may indicate low-density concrete with cracks or voids.

2.3.6 Unconfined Compression Test (UCT)

Unconfined compression tests (UCT) according to British Standard BS 1881: Part 116: 1983 were performed to measure the strength of all samples using a Dension 200KN universal testing machine. A cylindrical sample with length-to-diameter ratio equal to 2 was placed between two plates and a constant axial load applied at a constant rate until failure of the specimen occurred. The compressive strength of the specimen is calculated by dividing the maximum load attained during the test by cross-sectional area of the specimen.

The quality of the sample and suitable uses of the produced S/S system can be assessed using established limits (Table 2.2).

Table 2.2: Acceptable strength for disposal or re-use of (S/S) solidified waste

Management option	Min. value of UCS (MPa)	Reference
Safe waste land disposal	>0.30	NRC-US 1991 U.S EPA 2004 Qian et al., 2006
Produce blocks and fixing bricks	> 2.8	BS 6073-1:1981
Production of bricks	> 7.0	

2.3.7 Toxicity characteristic leaching procedure (TCLP)

Leaching to assess toxicity was undertaken according to British Standard BS EN 12457-1:2002. This determines the mobility of organic and inorganic chemical contaminants in the sample and whether leachates would classify the material as inert, non-hazardous or hazardous waste. It also assesses the risks that leachate could spread to the surrounding environment if disposed or re-used. Solid waste is exposed to a leaching solution under set conditions followed by physical and chemical analysis of the resultant solution (eluate). Results can be used to classify the toxicity of the solidified waste samples and to evaluate likely performance in selected waste management scenarios. Tests were conducted on particles of solidified waste <4 mm, exposure to 10 times its volume of deionised water and agitated for 24 hours under defined conditions (Table 2.3). The residue was separated initially by filtration through Whatman filter paper followed by membrane filtration (0.45 µm). The properties of the eluate were measured using standard methods for water analysis (ICP-MS, GC-FID and GC-MS).

Table 2.3: Leaching test parameters according to BS EN 12457-1:2002 (CEN, 2002).

Parameters	Conditions
Liquid: Solid ratio	10 L/kg
Sample weight	100 g
Type and volume of liquid	Deionised water 900 ml
pH	-
Agitation speed and period	10 rpm using an end-over-end mixer for 24 hours
Elute collection	Filtration through a 0.45µm membrane filter
Elute analysis methods	HMs by ICP-MS, TPHs by GC-FID

2.3.8 ICP-MS analysis

Elemental concentration in leachates, and solid materials after acid digestion ($\text{HNO}_3/\text{HClO}_4/\text{HF}$) were measured using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS, iCAP-Q Thermo Scientific) employing ceritas standard solutions for calibration and Ge, Ir and Rh as internal standards for drift correction.

2.3.9 Gas Chromatography GC-FID

Gas chromatography was used to identify and quantify total petroleum hydrocarbons (TPH) originating from samples containing drilling waste, and to evaluate the performance of selected waste treatment scenarios by measuring TPH in waste leachate using the parameters in Table 2.4.

Table 2.4: GC-FID operation condition according to EPA5201A

Instrument settings	Condition			
Pre-injection Delay time	0.0			
Post- injection Delay time	3.0			
Temp. Setting	200 °C			
Inlet Parameters				
Mode	Split less			
Split flow	41 ml min ⁻¹			
Splitless Time	1.0			
Purge Flow	6000 ml min ⁻¹			
Gas flow	25 ml min ⁻¹			
Oven setting				
	Retention Time (min)	Heating Rate (°C/min)	Target Temp. (°C)	Hold Time (s)
	0			
	30	0	50	3
	40	10	320	10

2.3.10 Gas Chromatography-Mass Spectroscopy (GC-MS)

Gas Chromatography-Mass Spectroscopy was used to identification and quantify TPH in methylene chloride extracts of drilling waste samples. Standard testing method USEPA 8270 was used to determine the concentration of (TPH) compounds in extracts prepared from both drilling waste samples. Samples were extracted with methylene chloride solvent DMC and dried using anhydrous sodium sulphate.

2.3.11 X-ray fluorescence (XRF)

X-Ray Fluorescence was undertaken using a PANalytical Axios advanced XRF spectrometer according to ASTM D8064 – 16 to identify the bulk composition of oxides present in the raw materials.

2.3.12 X-ray diffraction (XRD)

X-ray diffraction was used for determination of the amorphous nature of raw material, and to identify newly formed phases after the S/S reaction. Measurements were undertaken according to ASTM C1365 – 18 on a Hiltonbrooks PW1050 x-ray diffractometer using CuK α radiation (wavelength 0.15406 nm). Data processing and phase identification was done using Bruker DIFFRAC.EVA software and the ICDD PDF-2 2015 database. Samples were examined in the range 2θ , from 10° to 70° and in steps of 0.02/s.

2.3.13 Fourier transform infrared spectroscopy (FTIR)

Raw materials and final products were studied using FTIR (Bruker 27 TENSOR Series) to assess structural development, crystallinity and the degree of heterogeneity of solid samples. Infrared absorption bands enable the identification of specific molecular components and structures, the movement of bands present in the raw materials as well as the appearance of new bands in geopolymers can be attributed to the formation of new chemical compounds.

Samples were introduced as finely ground powders and characterized in the spectral range 500 and 4000 cm⁻¹. Table 2.5 lists characteristic bands used to detect changes in the microstructure of aluminosilicate materials (Handke, 1993)

Table 2.5: FTIR Band interpretation for raw materials and produced geopolymers

Wave No (cm^{-1})		Potential Origin
2800-3700	OH	Na-hydroxide, Ca-hydroxide and water
2860-2920	Aliphatic CH_3 & CH_2	Hydrocarbon contamination within drilling waste
2520	CO_3	Carbonate (drilling waste)
2340-2380	CO_2	Atmospheric CO_2
1790	CO_3	Na-Carbonate, Ca-Carbonate (from drilling waste)
1640	H-O-H	Structural Water
1440	CO_3	Na-Carbonate, Ca-Carbonate (from drilling waste)
1150	SiO_2	Quartz in original raw materials
1020	Si-O	Silicon dioxide (Quartz)
980-1000	Si-O-Si & Si-O-Al	Finger print of geopolymer matrix, existing aluminosilicate and quartz sand
930	Ca-Si-H	Calcium Silica hydrate
870	CO_3	Na-Carbonate, Ca-Carbonate (from drilling waste)
710	CO_3	Na-Carbonate, Ca-Carbonate (from drilling waste)
650-775	Al-O & Si-O	AlO_4^- , or SiO_4
579	Si-O-Si & Al-O-Si	Geopolymerisation

2.3.14 Ion Chromatography (IC)

Ion chromatography (Dionex ICS-1100, Sunnyvale, CA, USA) was used to measure the concentration of extractable anions (NO_3^- -N, SO_4^{2-} -S, Cl^- , F^- and PO_4^{3-}) in waste samples and soil according to ASTM D4327. The instrument was equipped with an anion self-regenerating suppressor column, flow-through pump and temperature-condensed conductivity detector. Analyte chromatograms were plotted, and data handled using Chromeleon software (version 6.80 SR6a).

2.3.15 pH measurements

The pH of waste samples, binders, native soil and leachate was measured according to British standard BS EN 15933:2012 using a pH meter (Mettler Toledo) after calibration at pH 4.0 and 7.0. Five grams of solid sample was placed in a 50 ml centrifuge tube and 25 ml deionised water added. Samples were shaken on an end over-end shaker for 60 minutes and the suspension allowed to settle for 1 hour prior to pH measurement.

2.3.16 Electrical conductivity (EC) measurements

Electrical conductivity (EC) of raw materials and solidified samples were measured according to ASTM D1125 using a conductivity cell (HANNA HI 9835 Microprocessor) by measuring the electrical resistance of a 1:5 solid: water suspension. Solution from leachability tests were measured by immersion of the conductivity cell in the solution.

2.3.17 Determination of Soil Moisture Content

Moisture content was determined according to BS 1377-2:1990 by adding 20 g of solid material (in triplicate) into weighed evaporating basins. Sample were placed in an air-circulating oven at 105°C overnight, cooled in a desiccator and re-weighed. Percentage soil moisture content was calculated from loss in weight.

2.3.18 Carbon measurement (TC, TIC and TOC)

Total carbon (TC), total organic carbon (TOC) and total inorganic carbon (TIC) was quantified using a Shimadzu Flash EA 1112 Nitrogen and Carbon analyser. Leachate samples were acidified before TOC was determined using a Shimadzu TOC-Vcph carbon analyser.

2.4 Phytoremediation Methodology

An assessment of the potential of Bermuda grass species *Cynodon dactylon* for the phytoremediation of drilling waste was undertaken. A 60-day pot experiment under controlled conditions to mimic the Libyan Desert environment tested the viability of phytoremediation of soils contains different amounts of drilling waste. Chemical analysis was used to assess the capability of the grass to remove accumulate heavy metals and remediate TPH. Rhizodegradation mechanism and the microbial activity in rhizosphere

soil was assessed using Biolog plates, also measurement of dehydrogenase activity (DHA) to evaluate the role of microbial enzymes in the breakdown of TPH conducted.

2.4.1 Materials

Soil and contaminated waste samples were collected as described in Section 2.2.1. They were then sieved to <4 mm to eliminate stones and plant material and thoroughly mixed to homogenise. Commercially available Bermuda grass (*Cynodon dactylon*) was sowed in pots contain native soil (control), and deferent soil contaminated by both types of drilling mud. A composite NPK fertilizer (N: P₂O₅: K₂O of 10: 8: 9) prepared from high purity potassium nitrate and phosphate salts (Fisher Scientific UK) was applied to enhance the natural fertility of the soils. Reagent grade dichloromethane and anhydrous sodium sulphate (Fisher Scientific, UK) were used for extraction of samples for GC-FID analysis and a high purity C8-C40 alkane calibration standard in dichloromethane (Sigma-Aldrich) was used for calibration of the GC-FID.

2.4.2 Phytoremediation experiments methods

2.4.2.1 Extraction of petroleum hydrocarbons

Samples for TPH analysis by GC-FID were extracted using three different approaches. Two grams of un-planted soil/waste mixtures from all treatments and rhizosphere soil from planted treatments mixed thoroughly with 3 g of anhydrous sodium before 10 ml of dichloromethane was added. After shaking for 15 min samples were centrifuged at 4000 rpm for 20 min and the supernatants transferred to amber glass vials and stored at 4°C until analysis using GC-FID. Leaf samples were ultrasonically extracted. Dried leaves were ground and mixed with anhydrous sodium sulphate to give a free-flowing powder. The mixture was extracted with 5 ml dichloromethane and placed in an ultrasonic bath for 10 minutes before centrifugation and storage in amber vials at 4 °C before analysis. Leachates were serial extracted using 2 x 5 ml dichloromethane in a separation funnel by allowing the aqueous and organic phases to separate, then removing the lower (organic) fractions through anhydrous sodium sulphate and

combining them before concentration to 5 ml using a rotary evaporator. All extracts were analysed by GC-FID according to the method described in Section 2.2.9. in Chapter 2.

2.4.2.2 Elemental analysis

Solid samples were prepared for ICP-MS analysis as described in Section 2.2.8. Leachate samples were analysed after acidification to 2% nitric acid. Plant samples (0.2 g) were microwave digested (Anton Paar) in Teflon vessels with 6 ml of HNO₃ before filtration and dilution to 2% nitric acid.

2.4.2.3 Biological analyses

Gram-negative Biolog plates (GN2) were used to evaluate the diversity and activity of microorganisms in the pot experiment after 60 days. In this technique, the rhizosphere soil extract solution was inoculated in Biolog plate wells contain different carbon sources and colourless tetrazolium dye and incubated at a constant temperature. During the incubation, soil microorganisms oxidize the substrates in the plate wells and, simultaneously, reduce colourless tetrazolium dye to a violet formazan. The intensity of violet formazan colour is measured spectrophotometrically and used as indication of microbial respiration. The formation of a purple formazan colour and its intensity is used as indication of microbial respiration and the amount of substrate utilized reflects the extent of microbial community activity and its diversity (Zak et al.,1994; Garland, 2006). Intensity readings that were greater than 40 % of the control well reading (Well No.1 containing only pure water) were considered positive for substrate utilisation.

In this test, Soils were processed by undertaking a 10⁻² soil suspension dilution. Triplicate aliquots of 30 ml were poured into a sterile petri dish before 100 µl aliquots were placed into the wells of Biolog plates. The plates were incubated at 25°C for 72

hours and assessed every 24 h. Absorbance at 590 nm was measured using a Spectramax M5 (Molecular Devices).

The results were used to measure **average metabolic response** (AMR) which describes the average respiration of the C-sources by the microbial community and provides a single metric by which communities can be compared. The AMR is calculated as the average of the mean difference between the O.D. of the C-source-containing wells and the control well using the following equation:

$$AMR = \frac{\sum(OD\ well - OD\ control)}{95}$$

Where, (*O.D. well* – *O.D. control*) is the optical density of each carbon source containing well minus the O.D. of the negative control well.

The **community metabolic diversity** (CMD) is represented by the number of substrates utilized by the microbial community and used to evaluate the efficiency of substrate mineralization by soil microorganisms and. reveal the factors regulating microbial respiration (Ferreira et al, 2012) The CMD is calculated by summing the number of positive responses (purple-coloured wells) observed following incubation. A threshold O.D. must be established above which the purple coloration indicates a usage of the carbon source by the microbial community. This threshold is commonly set at O.D. = 0.25. observed following incubation (Vahjen et al., 1995).

Average well color development (AWCD) was used for monitoring of the color development of all wells of a plate during the incubation period resulted from consumption of C-source in each treatment (Zak et al., 1994; Deng et al., 2011).

2.4.2.4 Dehydrogenase activity measurement (DHA)

Measurement of dehydrogenase activity (DHA) is an indicator of soil quality change resulting from phytoremediation. Dehydrogenase enzymes in the soil play an important

role in biochemical reactions taking place in the rhizosphere and are linked to redox process needed for oxidation of the hydrocarbons present (Utobo and Tewari, 2014).

To determine DHA, the modified method of (Thalman, 1986) was used. The colourless water-soluble dye triphenyltetrazolium chloride (TTC) used as an indicator of electron transport system (ETS) activity. In the presence of dehydrogenase enzymes TTC is reduced to insoluble red coloured triphenyl formazan (TF), which can be extracted and quantified calorimetrically. Five grams of control and planted rhizosphere soil was mixed with 5 ml of 0.1% w/v TTC dissolved in Tris buffer and incubated for 16 h in 25 °C in the dark place. After the incubation 25 cm³ methyl alcohol was added and the samples were thoroughly mixed for 2 h in the dark before filtration through (Whatman filter papers) into a 50 cm³ volumetric flask and made to the mark with methyl alcohol. The absorbance was measured on a spectrophotometer (CE1011 Cecil Instruments) at a wavelength of 524 nm.

2.4.2.5 Leaf area measurements

Leaf area measurement is important for the assessment of the effect of environment and climate on the growth of plants, including the cumulative effects of nutrients and contaminants uptake over the growth period. Leaf area was measured using a LI-3100C Area Meter by passing samples under a light source.

2.5 Statistical analysis

GENSTAT (13th Edition Lawes Agricultural Trust, Rothamsted Experimental Station; 2015) was used to analyse data using standard analysis of variance (ANOVA). Probability values of 0.05 or less ($P < 0.05$) were taken to be significant. Treatment means were compared using least squares deviation of the means using Duncan's Multiple Range Test.

Chapter 3: Solidification/Stabilization of drilling waste utilizing industrial by-product based geopolymers

3.1 Introduction

Solidification/stabilization (S/S) is one of the most widely used approaches for the management/disposal of contaminated media and waste; particularly materials classified as hazardous and contaminated with heavy metals, hydrocarbons or radioactive nuclides (Conner and Hoeffner, 1998). The U.S. Environmental Protection Agency (EPA) considers S/S an established treatment technology, defining the **stabilization processes** the reduction of the hazard by impeding the mobility of contaminants, converting them into less soluble forms, and the **solidification processes** is the way in which the waste is chemically encapsulated forming a solid material (EPA 1991).

The combined process of S/S mixes contaminated material with treatment agents (binders and additives) targeting immobilise, both physically and chemically, the hazardous constituents. Additives are chemicals that stabilize the contaminants by converting them to more stable forms and binders are used to solidify the materials together forming a solid matrix (Bougharraf et al., 2018). The final product of S/S can be a monolithic block, a clay-like material, a granular particulate, or other physical forms that meet the requirements of safe waste management options such as storage, landfilling or re-use in a beneficial way (Rani et al., 2017).

Ordinary Portland Cement (OPC) is the most commonly used binder as it has a relatively low cost and is widely available, although hydrated lime is also used (Kundu et al., 2008; Moon, 2004). In recent years, to reduce pollution from cement manufacturing operations, many studies have considered using geopolymers as an environmentally sustainable alternative to cement. Geopolymer concretes have comparable strength to OPC based concretes, and are produced using aluminosilicate base materials derived

from industry by-products e.g. Ground granulated blast-furnace slag (GGBS) (Deevasan, 2011), fly ash (Skvara et al., 2006), or the remains of industries based on clay materials such as brick and masonry (Duxsons et al., 2007a). Geopolymer concretes also have low shrinkage and are acid resistant (Mehta and Siddique, 2017). They have been used successfully for the fixation of heavy metals and radioactive materials present in different types of waste, but little work has been done to describe and evaluate the potential of utilizing geopolymers for the treatment of complex industrial wastes such as drilling waste from the oil industry that contains significant percentages of petroleum hydrocarbons (TPH) and heavy metals (HMs).

Organic contaminants such as TPH have deleterious effects on the classical OPC concrete hydration process (Paria and Yuet, 2006), with observable effects at concentrations as low 3 wt.% of petroleum hydrocarbons (Ho, 2017). However, there is little available research on the effect of hydrocarbons on geopolymer concrete strength. Whilst it is anticipated that the effects will be similarly deleterious (as the activation process of geopolymers still requires water as solvent and media for dissolution) it is theorized that due to the different chemical processes the geopolymer concretes may be able to withstand higher concentrations of hydrocarbons.

The objective of the work presented in this chapter, therefore, was to systematically investigate the ability of geopolymers, prepared using industrial by-products such as brick industry waste and steel industry waste and discussing their effectiveness as binders to successfully stabilize and solidify drilling waste from the oil industry. This type of geopolymer has not been previously investigated.

3.2 Materials and Methods

3.2.1 Materials

Two drilling waste samples (WBM and OBM) comprising soil and waste mixtures, and uncontaminated soils were sampled and prepared as described in Section 2.1.1 in

Chapter 2. The physical properties, chemical composition, and leachability properties are given in Table 3.3.

Two different industrial by-products were used to prepare geopolymers with drilling waste. Steel industry waste (SI) and Brick industry Remains (BR) produced under high temperature conditions (1000-1650°C) are both considered as industrial waste in Libya. Steel industry waste was collected from the Musrata Iron and Steel Complex and BR was sourced from the scrapyards of Zliten Brick factory. Portland cement type I (PC) was obtained from Alburg manufactory (Zliten, Libya) was used as a traditional binder for comparative purposes. The physical properties and chemical composition of all binder materials are given in Table 3.4.

A sodium hydroxide with high purity manufactured by Fisher Scientific UK was used as alkali activator for proposed geopolymers.

3.2.2 Experimental design and methods of analysis

Whilst there is a large body of research on the use and development of geopolymer technologies for the treatment of waste containing heavy metals or radioactive elements, there is currently little research into its application for treatment of oil drilling waste contaminated with hydrocarbons and heavy metals. The studies that exist have been conducted on synthetic samples (Al-Ansary et al., 2007; Masrulita et al., 2018) or used very high binder contents (Tuncan and Koyuncu, 2000), neither of which are economically viable or entirely applicable. Therefore, in this work, the focus has been on developing a recipe that is easily transferrable to the field by using real drilling waste samples and locally available additives. The objective was to maximise waste and minimise binder contents to produce a viable product and to compare that to equivalent materials produced using OPC. The bulk composition of the recipe tested is given in Table 3.1.

The binder content 25% OPC content in proposed recipes was selected based on the recommendation by Al-Ansary and Al-Tabbaa, (2007) and Antimir et al., (2010) to convert drilling waste to non-hazardous waste acceptable for safe landfill in the UK (EBPRI 11507B, 2013), or to obtain the minimum requirements for compressive strength (0.3 MPa) for disposal wastes in the land according to the (NRC., 1991; EPA, 2004) as recommended by Al-Kindi, (2019).

Table 3.1: Bulk composition of drilling waste concrete tested.

Constituent	wt. %
Binder	25
Aggregate	15
Drilling Waste/control Sand	40
NaOH/water	20

Using these proportions, nine combinations were tested (Table 3.2).

Table 3.2: Composition of steel industry waste (SI), brick waste remains (BR) and Portland cement (PC) concrete combinations tested using uncontaminated soil, water (WBM) and oil (OBM) based mud contaminated soils.

Soil/Waste	Binder	Code
Native soil	SI	SI-C
WBM	SI	SI-W
OBM	SI	SI-O
Native soil	BR	BR-C
WBM	BR	BR-W
OBM	BR	BR-O
Native soil	PC	PC-C
WBM	PC	PC-W
OBM	PC	PC-O

The binder and soil/drilling waste were mixed thoroughly in a Kenwood mixer at 140 RPM for 5 minutes before gradually adding the activation solution or water with continued mixing for a further 10 minutes before the aggregate was added. After mixing, the mix was poured into pre-prepared 50 x 200 mm cylindrical HDPE moulds for later measurement of UPV and UCT, and 10 x 35 mm cuboid polystyrene subsamples moulds for measurement of other properties including leachability. Once in the mould, samples were shaken for 5 minutes to allow settling and remove air bubbles. The mould designs are shown in Figure 3.1.

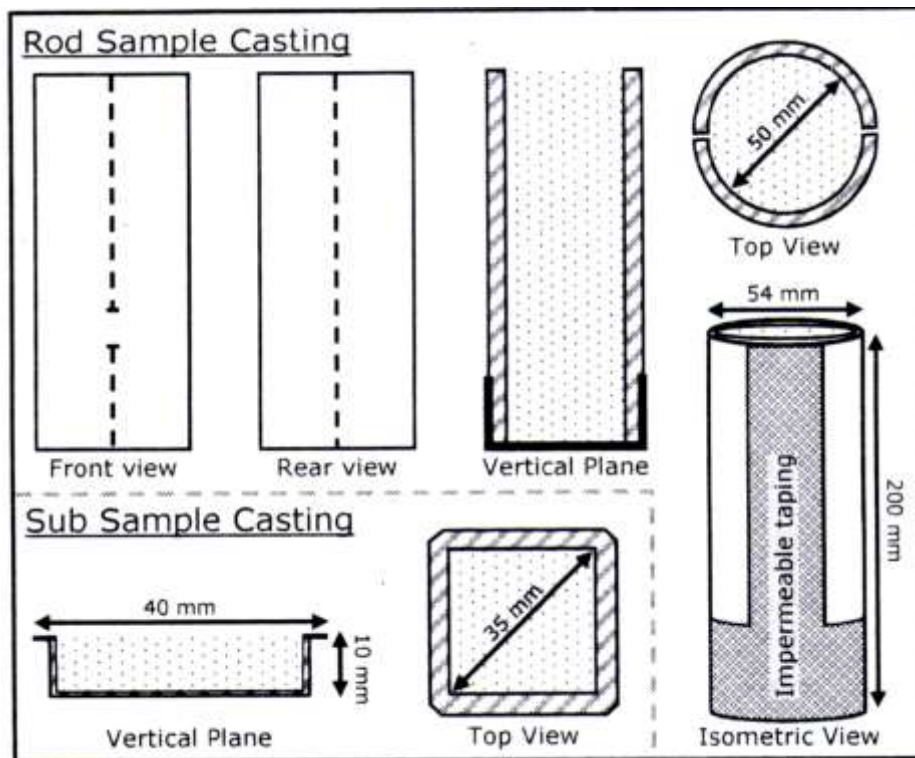


Figure 3.1. Schematic drawing of moulds used to manufacture the concrete samples.

Samples were cured in an incubator under conditions typical of the Libyan Desert in July (table 3.3) after consideration of weather data for the Jalu area (Worldweatheronline.com 2018) over one year (2018). All samples were cured for 56 days with a relative humidity of more than 50%.

Table 3.3: Programmed daily temperature regime for Jalu, Libyan Desert during July.

Time	5 am	8 am	11 am	2 pm	5 pm	8 pm	11 pm	2 am
Temperature (°C)	26	29	34	38	39	34	31	28

3.2.3 Leaching

TCLP Leaching test was undertaken according to British Standard BS EN 12457-1:2002 as described in Section 2.3.1.3, Chapter 2 to determine the leachability of the heavy metals and petroleum hydrocarbon. Elemental analysis of the leachates used ICP-MS

as described in Section 2.2.8, Chapter 2. Total organic carbon analysis was undertaken as described in Section 2.2.18, Chapter 2.

3.2.4 Durability Testing

Ultrasonic pulse velocity testing (UPV) as described in Section 2.2.5, Chapter 2 was used to examine the homogeneity, and predict the strength, of samples cast whilst avoiding their destruction. Testing was undertaken after 3, 4, 5, 6, 7, 14, 21 and 28 days. After one month monitoring the changes measured by UPV, the 200 mm rod samples were cut into four 40 mm sections for unconfined compression testing (UCT) as described in Section 2.2.6 in Chapter 2 to provide ultimate strength at days 28 and 56.

3.3 Results and Discussion

3.3.1 Characterisation of the soil and drilling waste

The characteristics of the untreated drill cuttings, including their physical properties, bulk chemical composition, organic carbon analysis, heavy metals content and leachability are summarized in Table 3.4. The results were compared with the criteria for granular waste acceptable at landfills proposed by the UK environment protection agency (EBPRI, 2013) shown in table 3.4 to enable qualitative and quantitative assessment of the drilling waste samples.

In general, the soil-based drilling waste samples (WBM & OBM) were characterized by a slightly basic pH and rated as weakly saline soils (2-4 ds m⁻¹). Both samples had a loamy-sand texture with clay content (5-8%). Both samples had a fine

particle size resulting in a high specific surface area of 2043 for WBM and 3173 cm² g⁻¹ for OBM. X-ray diffraction indicated that the uncontaminated soil was primarily composed from quartz, whereas WBM composed from quartz and calcite (CaCO₃) and

minor amounts of ankerite ($\text{Ca}(\text{Fe}^{+2},\text{Mg})(\text{CO}_3)_2$), and OBM composed from quartz, calcite and contained barite BaSO_4 .

The TOC content of OBM at 8.56 wt. % exceeds the 6 wt. % danger level for hazardous waste landfill. The TOC of WBM and native soil was 1.47 wt. % and 0.015 wt. % respectively classifying WBM in the inert waste landfill category. Petroleum hydrocarbon content of both drilling waste samples indicated high contents of fraction 2 (C10-C16) and fraction 3 (C16-C34) hydrocarbons, which correspond to those of gasoline and diesel fuel respectively (Bogusz, 2008). According to published literature, the lighter fractions (F2) result in acute toxicity due to their high-water solubility and bioactivity, whereas the higher molecular weight compounds in fraction 3 are not highly toxic but are very hydrophobic and resistant to degradation (Khan et al., 2018).

Chemical characterization of the drilling waste samples shows that Ca, Si and Al are the most common constituents but that waste samples also contained As, Cd, Co, Mo, Se, V, Pb, Cu, Zn, Ni, and Cr (Table 3.3). Elemental concentrations with the exception of Zn in WBM, were following the upper limits allowed in soil disposed of as fill material (APPENDIX 1) (appendix 1). TCLP Leachability test (Table 3.4) demonstrated that most elements in the drilling wastes were unlikely to leach from the samples thus, they are unlikely to pose a concern.

Leachability tests did however demonstrate significant organic hydrocarbon leachate with 5135 and 12963 mg kg^{-1} released from WBM and OBM respectively, both of which exceed the maximum level allowed for landfill of 500-800 mg kg^{-1} (APPENDIX 1) (Table 3.4), meaning that both waste types are classified as hazardous waste and require treatment before disposal.

Table 3.4: Comparison of leachability of drilling waste samples compared with the criteria for granular waste acceptable at landfills (UK Environment agency) (Appendix1)

Parameter	Unit	WBM	OBM	Native Soil	Inert Waste landfill	Stable nonreactive hazardous waste (SNRHW)	Hazardous waste landfill
Physical Analysis							
pH		8.4	8.80	8.7		>6	
Conductivity	mS cm ⁻¹	4.2	4.06	0.08			
TDS	mg kg ⁻¹	1995	2035	38	4000		
Moisture	wt. %	55.2	12.4	3.79			
LOI	wt. %	59.5	21.3	4.35			10
Mean Particle Size	µm	314	193	124			
Specific Surface Area	cm ² g ⁻¹	2043	3173	795			
Clay	wt. %	7.46	4.97	0.02			
Silt	wt. %	14.5	16.6	3.40			
Sand	wt. %	78.0	78.4	96.2			
Soil Classification		Loamy Sand	Loamy Sand	Sand			
XRD Analysis							
Minerals identification		Quartz, calcite, Ankerite	Quartz, calcite, baryte	Quartz			
Organic analysis							
TOC	wt. %	1.47	8.56	0.015	3	5	6
C6-C10	wt. %	0.0	0.0	-			
C10-C16	wt. %	24.3	27.2	-			
C16-C34	wt. %	75.7	72.8	-			
Elemental Analysis							
SiO ₂	wt. %	23.61	19.20	83.74			
TiO ₂	wt. %	0.24	0.10	0.66			
Al ₂ O ₃	wt. %	3.34	4.20	5.14			

Fe ₂ O ₃	wt. %	1.72	1.85	1.71			
MnO ₂	wt. %	0.01	0.01	0.06			
MgO	wt. %	3.05	0.67	0.91			
CaO	wt. %	32.60	27.2	1.93			
Na ₂ O	wt. %	0.82	0.40	0.44			
K ₂ O	wt. %	0.34	0.39	1.59			
Ni	mg kg ⁻¹	8.4	19	5.25			
Cu	mg kg ⁻¹	9.3	34.5	16.4			
Zn	mg kg ⁻¹	50.9	74.8	19.3			
As	mg kg ⁻¹	2.01	6.17	1.37			
Cd	mg kg ⁻¹	0.44	0.72	0.04			
Ba	mg kg ⁻¹	1066	3832	242			
Pb	mg kg ⁻¹	10.3	61.0	7.07			
Leachability Analysis							
TOC	mg kg ⁻¹	5135	12963	355	<500	800	1000
V	mg kg ⁻¹	0.16	0.19	0.12			
Cr	mg kg ⁻¹	0.11	0.02	0.1	0.5	10	70
Ni	mg kg ⁻¹	0.08	0.19	0.09	0.4	10	40
Cu	mg kg ⁻¹	0.12	0.4	0.70	2	50	100
Zn	mg kg ⁻¹	8.19	0.12	5.41	4	50	200
As	mg kg ⁻¹	0.04	0.02	0.02	0.5	2	25
Cd	mg kg ⁻¹	0.0	0.0	0.0	0.04	1	5
Ba	mg kg ⁻¹	0.45	10.3	0.38	20	100	300
Pb	mg kg ⁻¹	0.01	0.03	0.11	0.5	10	50
Cl	mg kg ⁻¹	6590	8400	82	800	15000	50000
SO ₄ ²⁻	mg kg ⁻¹	2152	303	20	1000	20000	50000

3.3.2 Characterisation of the binders

The chemical composition of BR and SI were analysed by X-ray fluorescence and the results are shown in Table 3.5. The main components of BR are SiO₂ and Al₂O₃, which account for 84.30%. The main components in SI are MgO and CaO, accounting for 90.02 %. The SiO₂ and Al₂O₃ content in SI very low comparing with BR.

Table 3.5 Physical properties, chemical composition and XRD analysis for used binders

Parameter	Units	OPC	BR	SI
<i>Physical Properties</i>				
pH	-	12.5	9.90	9.5
Conductivity	ms cm ⁻¹		0.88	0.72
<i>XRF analysis</i>				
SiO ₂	wt. %	21.2	69.10	1.16
TiO ₂	wt. %	0.32	0.93	0.09
Al ₂ O ₃	wt. %	5.43	15.20	0.69
Fe ₂ O ₃	wt. %	3.68	5.75	4.54
Mn ₃ O ₄	wt. %	0.02	0.04	0.59
MgO	wt. %	1.76	1.43	81.23
CaO	wt. %	64.5	1.78	8.79
Na ₂ O	wt. %	0.10	0.26	<0.01
K ₂ O	wt. %	0.73	2.80	<0.003
P ₂ O ₅	wt. %	0.17	0.13	0.04
SO ₃	wt. %	1.54	0.39	0.02
LOI	wt. %	1.32	1.21	3.03
<i>XRD Analysis</i>				
OPC	Calcite CaCO ₃ , calcium silicate Ca ₃ SiO ₅ , lamite Ca ₂ SiO ₄ , brownmillerite (Ca ₂ (Al,Fe ⁺³) ₂ O ₅)			
BR	Calcite CaCO ₃ , quartz SiO ₂ , hematite Fe ₂ O ₃			

3.3.3 Solidification

From all the nine recipes tested (Table 3.2), only two recipes (BR-W, PC-W) were sufficiently solidified that they could be removed from the moulds in one piece. The samples produced using SI as a binder (SI-C, SI-W and SI-O) or prepared using OBM waste (BR-C, BR-O and PC-O) failed to produce solid matrixes of a reasonable strength. The failure of these mixtures may be attributed to one or more factors including existence of a high quantity of unreactive silica (crystalline form) not in amorphous form in both drilling waste samples and binders, sub-optimum molar ratios of key constituents, an alkali-silica reaction occurring, insufficient available water and the presence of large quantities of petroleum hydrocarbons.

No published studies were found that recommended optimum oxide proportions for geopolymer mixtures composed from SI or BR waste materials with drilling waste contains petroleum hydrocarbons. Information on the formulation of geopolymer using metakaolin (MK), steel industry waste (IS) and fly ash (FA) as the aluminosilicate material used for S/S treatment for different waste contains heavy metals or radioactive materials suggests that the optimum molar ratios to achieve highest strength and durability are:

(3.0-3.8) $\text{SiO}_2:\text{Al}_2\text{O}_3$, (1-1.2) $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ and (10-11) $\text{H}_2\text{O}:\text{Na}_2\text{O}$.

Comparison of the formulations tested here with the optimum molar ratios for geopolymers based on metakaolin and fly ash (Table 3.6) suggests that the $\text{SiO}_2:\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}:\text{SiO}_2$ molar ratio selected far exceed the idealised proportions recommended in different published studies (Davidovits 2008; Rowels et al., 2003; Kamalloo et al. 2010; Zhuang et al. 2016).

Ghosh and Paratha, (2012) concluded that using a $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio > 4.0 (based in the amount of reactive silica incorporated in formation of geopolymer gel) inhibited the geopolymerisation process. Rowles et al., (2009) also observed that exceeding a ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ of 3.8 (based in quantity of reactive silica) resulted in a decline in the binding characteristic of geopolymers and formation of very pore geopolymer structure with very low mechanical properties.

As a result, it is likely that geopolymers using SI and OBM formed with poor structure, primarily due to the deficiency of Al_2O_3 and the excess of SiO_2 resulting in a high $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio. The XRD analysis results shown in table 3.4 and table 3.5 show that drilling waste samples and binders contain a high amount of silica in quartz form. Quartz is the most common form of crystalline silica considered as unreactive silica. The existence of high amount of quartz in geopolymer systems lead to increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the geopolymer matrix, slowing the dissolution of Si and Al compounds at ambient temperature, and adsorption of a large quantity of water and

associated with formation of looser structure of the geopolymer matrix due to the increased amount of unreacted materials as reported by Patel and Shah (2018).

Table 3.6. Comparison between oxide ratio within the produced geopolymer systems and that recommended in the literature review (after Davidovits, 2008, Rowels et al., 2003 and Zhuang et al., 2016).

S/S System	SiO ₂ :Al ₂ O ₃	Na ₂ O:Al ₂ O ₃	Na ₂ O:SiO ₂	H ₂ O: Na ₂ O
SI-C	25.4	3.50	0.147	10.6
SI-W	10.8	5.30	0.492	10.3
SI-O	8.40	2.90	0.353	10.3
BR-C	8.70	1.40	0.167	10.2
BR-W	8.10	1.20	0.147	10.2
BR-O	13.9	1.20	0.100	10.5
Recommended range:	3.0-3.8	1-1.2	0.30	10-11

Another possible explanation for the failure of formation of geopolymer gel in proposed systems is the presence of large amounts of silica under extremely alkaline condition (i.e. an excess of NaOH) which result in an alkali-silica reaction (ASR). This is where a reaction between alkalis (Na₂O and/or K₂O) from cement or other sources and certain reactive silica minerals present in the system take place in presence of water. The chemical reaction results in abnormal expansion and cracking of concrete alkali silicate gel which has a significant ability to absorb water molecules inducing expansion and micro-cracking inside the structure of the solids produced (Frany and Kosmatka, 1997); Siddique and Cachim, 2018). This reaction also causes significant and irreversible damages in structures due to swelling of the concrete as reported by Central et. al, (2017). This ASR reaction also reduces the quantity of water required for dissolution of starting materials and the formation of geopolymer gel, affecting the entire geopolymer formation process (Zuhua et al., 2009). The shortage of water in cement systems also leads to a decrease in the binding capacity of cement resulting in loose and incoherent systems (Živica ,2009).

For samples containing a high concentration of petroleum hydrocarbons (SI-O, BR-O and PC-O), the higher concentration of TPH within the mixes (8.56 wt. % TOC) may have been sufficient to form a hydrophobic barrier around the grains of drilling waste, thereby preventing the hydration reaction in the cement system and alkali activation of the aluminosilicate which is the important step in the geopolymerisation reaction.

Ghasemi et al., (2017) reported a similar destructive effect of petroleum hydrocarbons in decreasing the efficiency of the S/S process.

The BR-W and PC-W systems produces solid matrixes with acceptable strength probably as a consequence of their lower TPH content which allowed the formation of geopolymer gel within the BR-W system and facilitated the hydration reaction within PC-C and PC-W systems. Also, the presence of a greater Al_2O_3 content in BR reduces the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio allowing the formation of more geopolymer gel which reflects positively in the mechanical properties of this system.

Ultrasonic pulse velocity (UPV) testing was used to assess the relative quality and uniformity of the solidified systems (BR-W, PC-C and PC-W) whilst curing for 28 days (Figure 3.2). All solidified samples had pulse velocities below 2100 m s^{-1} during the 28-day testing period indicating that they were of poor quality when compared with concrete according to the criteria suggested by Whitehurst, (1966). Initially, all samples appeared to maintain or gain quality for the first 7 days, however, after 10 days, all deteriorated. Deteriorating velocity speeds are theorised to be a result of incompleteness of geopolymerisation or hydration reactions and the subsequent developments of fractures and flaws within the internal structure of the systems.

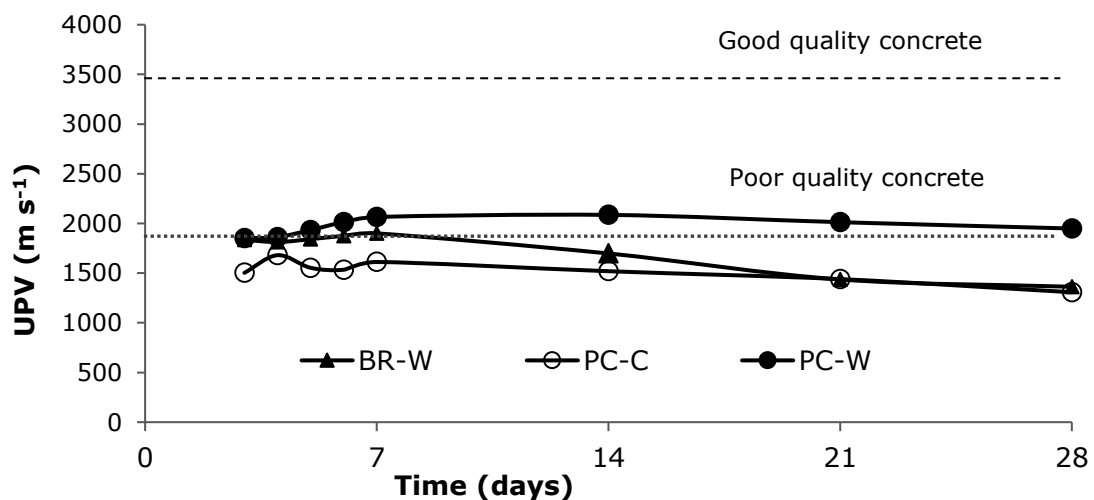


Figure 3.2: Change in UPV speeds for solidified samples over a 28-day curing period. Concrete quality standards (shown as dashed lines) are those recommended by Whitehurst (1951).to predict the quality of concrete

Unconfined compression testing of samples BR-W and PC-W (Figure 3.3) shows that the compressive strength testing of BR-W and cement concrete PC-W for 28 days cured samples at similar media were slightly different after 28 and 56 curing period. BR-W show compressive strength values higher than OPC concrete. Both systems show deterioration if strength after 56 days which confirm the results obtained by measuring the UPV test.

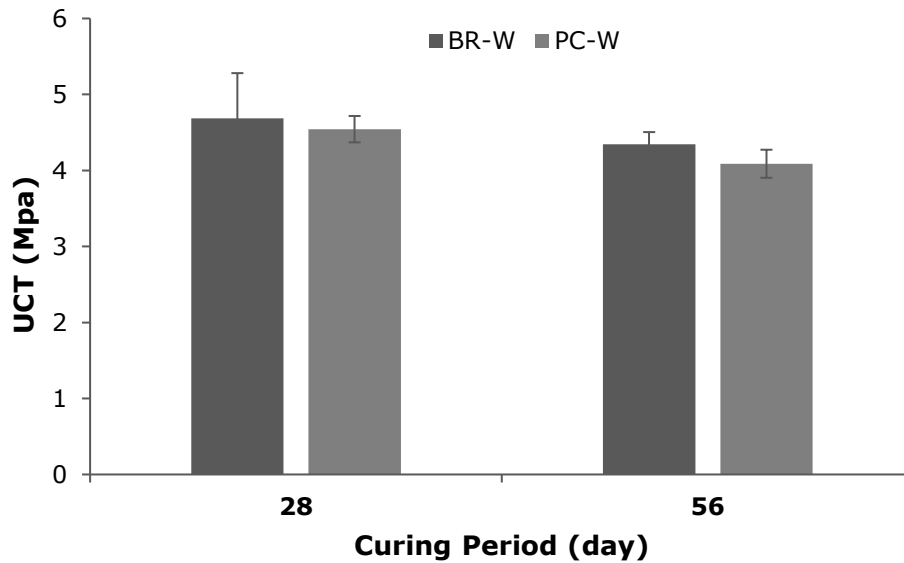


Figure 3.3: Ultimate strengths of binder-waste systems at 28- and 56-days intervals. Error bars represent the standard deviation values obtained by triplicate samples

The reduction in the UCT in both systems between day 28 and day 56 was ~9 % for BR-W system and ~19% for PC-W and likely results from incompleteness of geopolymerisation reaction in BR-W and poor hydration in PC-W system, or alkali-ASR occurring. The results support the finding of the UPV testing and confirm the deterioration in internal structural in both systems with time and the detrimental effect of this on mechanical strength.

3.3.4 Stabilization

Leachate from both BR-W and PC-W was highly alkaline, with pH values of 12.1 and 12.5 respectively. Alkalinity was also substantial at 253 meq. L⁻¹ for BR-W and 260 meq. L⁻¹ for PC-W. Results in Table 3.7 indicate substantial Na⁺ in the leachate of all solidified systems and together the high pH values and Na concentration is likely to

indicate excess NaOH (alkali activator) and result from gradual deterioration on the solidified systems due to the detrimental effect of formation of ASR gel in these systems. The results also demonstrate that the amount of Al and Ca in the leachate is low which is attributable to the consumption of all available Al and Ca in the starting materials and formation of an insoluble form compounds.

Table 3.7: Elemental concentrations in leachate from solidified samples compared with the criteria required to be met for leachate from inert waste that are acceptable at landfill (Appendix 1).

System	Na	Al	Ca	V	Cr	Mn	Cu	As	Ni	Cd	Pb
BR-W	56516	88	23.5	13.8	0.27	0.20	2.0	1.3	0.20	0.0	0.02
PC-W	54895	296	23.0	4.90	1.58	0.02	0.6	1.0	0.38	0.0	0.13
<i>Criteria for granular waste acceptable at landfills</i>											
Inert waste					0.5		2.0	0.5	0.4	0.04	0.5
Stable nonreactive hazardous waste			NL		10.0	NL	50	2	10	1	10
Hazardous waste landfill					70.0		100	25	40	5	50

NL = not listed

Comparison to the UK Environment Agency criteria (Appendix 1) for the acceptance of inert waste at landfill, shows that As and Cu concentrations in the leachate from the BR-W system and concentrations of As, Ni, and Cr in the PC-W system were above the acceptable levels. for inert waste landfill.

The leachability of petroleum hydrocarbons from samples of BR-W and PC-W also failed to meet the relevant inert waste criteria for landfill (Table 3.8). There was therefore a complete failed of both systems to convert the drilling waste to inert material acceptable for safe landfill management.

Table 3.8 Comparison of organic leachate generated by solidified samples of BR-W and PC-W with the unsolidified waste material (WBM). The landfill waste criteria (EBPRI, 2013) is 800 mg kg⁻¹.

Test	TPH leachate Conc. (mg kg ⁻¹)
WBM raw (untreated)	5135
BR-W	3400
PC-W	3700
<i>Criteria for granular waste acceptable at landfills</i>	
Inert Waste Landfill	500
Stable nonreactive hazardous waste & nonhazardous waste co-disposed with (SNRHW)	800
Hazardous waste landfill	1000

Furthermore, visual inspection on the solidified materials indicated the formation of a white surface precipitate on the solidified samples. This efflorescence phenomenon in cement concrete and geopolymers is an indicator of internal structural weakness (migration/degradation of component materials). For example, Zhang et al., (2014) found that the binder can influence the formation of efflorescence products in the solidified material resulting in negative effects on the compressive strength development of geopolymers. Efflorescence is caused by the presence of unreacted sodium oxide and/or the migration of dissolved salts within a porous material to its surface, where the water evaporates and salts precipitate, leaving a white layer composed of alkali carbonates and/ or bicarbonates as reported by Najafi et al., (2012) .

The leachability tests and the tendency of both solidified systems towards the formation of efflorescence confirmed the results of the solidification investigation wherein the negative effect of using an inappropriate starting material ratio results in weak mechanical strength. Neither of the solidified materials BR-W or PC-W produced materials suitable for environmental applications and in all systems, there was a failure to form solid matrixes capable of encapsulating the petroleum hydrocarbons due to the inappropriate selection of starting materials resulting in the formation of a porous matrix with poor physico-mechanical properties.

3.4. Conclusions

This chapter attempted to examine the ability of the industrial by-products steel industry waste and brick industry remains to be used as aluminosilicate materials for the formation geopolymers to solidify and stabilize drilling waste and immobilise the heavy metals and hydrocarbons they contain. The failure to achieve this objective highlights the importance of using appropriate SiO_2 : Al_2O_3 , Na_2O : SiO_2 , Na_2O : Al_2O_3 molar ratios, alkali activator concentration and water: solid ratios. The recipes tested did not have appropriate SiO_2 : Al_2O_3 mole ratios, a shortage of water and/or an excess of alkali activator. Furthermore, the presence of organic contaminants was observed have an equally negative impact on both the geopolymer and Portland cement-based samples. As a result, only 2 of the 9 proposed recipes (BR-W & PC-W) solidified to the extent that they could be tested for durability and leaching behaviour. Both systems failed to solidify the drilling waste contains high concentrations of petroleum hydrocarbons in OBM waste.

It is likely that the non-ideal SiO_2 : Al_2O_3 , Na_2O : Al_2O_3 and Na_2O : SiO_2 molar ratios observed within the proposed recipes and existence of unreactive silicate (quartz) in raw materials led to a reduction in the formation of the geopolymer network (Rowles et al., (2009); Kamalloo et al., (2010); Heah et al., (2013); Cho et al., (2017)). Consequently, geopolymer with poor microstructure and lower mechanical strength were obtained. Further work is therefore required to refine the S/S recipes and test the potential of geopolymer technology as a remedial solution for such a complex type of waste. This refinement is most likely to be achieved through the use of aluminosilicate materials with higher Al_2O_3 content to optimise the SiO_2 : Al_2O_3 ratio, reduction of the alkali activation concentration to the level where it can play its role in the formation of geopolymer gel with better microstructure and not result in the formation of efflorescence. Also, it is likely that a reduction in the amount of petroleum hydrocarbons in the drilling waste will be required to achieve solidification/stabilisation.

Chapter 4: The potential use of kaolin and metakaolin in S/S of drilling waste

4.1 Introduction

In recent years, geopolymers have been used as sustainable alternative binders in solidification/stabilisation waste management strategies and appear to compare favourably with traditional lime and cementitious materials (Zhang et al., 2012; Li et al., 2019). Geopolymers are characterised by their ability to cure at ambient temperature, their low shrinkage and permeability, good resistance to heat, tolerance of freeze–thaw cycles, chemical resistance and excellent durability (Majidi, 2009).

Geopolymers are obtained by the mixing of natural materials, minerals or industrial by-products that are rich in silicate and aluminate precursors with an alkaline activator such as sodium or potassium hydroxide or sodium or potassium silicates, which through a series of reactions (dissolution, gelation, reorganisation, polymerisation and hardening) at low temperature (<100°C) leads to the formation of solid materials (Morsy et al., 2014; Živica Palou and Križma, 2015).

Geopolymer technology has been developed and used as a sustainable alternative to the use of OPC in concrete for many civil applications. For example, Davidovits, (2015) used kaolin and calcined kaolin (metakaolin) as sources of aluminosilicate materials to synthesize and produce geopolymers for construction applications. Balaguru et al., (1997) used geopolymers for repair and rehabilitation of reinforced concrete beams, Shaikh et al., (2018) found that geopolymers can be used effectively in production of fireproof coating and production of composites materials, Liew et al., (2017) used geopolymers to produce ceramics and bricks for civil purposes, Gargav et al., (2016) produced geopolymers with excellent mechanical proprieties for road construction and Ricciotti et al., (2017) used geopolymers as restoration materials in cultural heritage projects.

Kaolin and metakaolin based geopolymers have become realistic and attractive materials worldwide due to their availability and low cost of manufacture from raw materials compared with geopolymers using more traditional binders (El-Eswed et al., 2015; Li et al., 2019). Kaolin is a natural material and a good starting material for the synthesis of geopolymers due to its high content of both silica (SiO_2) and aluminium oxide (Al_2O_3). The main constituent of kaolin clay is the mineral kaolinite with chemical formula ($2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) and a SiO_2 : Al_2O_3 molar ratio of 2. Calcination of kaolin clay between 550-800°C, produces metakaolin clay with a higher quantity of aluminate and slightly lower SiO_2 : Al_2O_3 ratio (~1.8) by removing internal structure water at high temperature (Kenne et al., 2015).

Extensive research has already been carried out exploring different types of industry by-products together with calcined clay for stabilising hazardous waste contain heavy metals and radioactive nuclides. Tian et al., (2019) and Qi et al., (2019) found that iron slag made an important contribution in solidification/stabilization of heavy metals in industrial waste. Baykal and Saygılı, (2011) reported that production of fly ash geopolymers helped to reduce the radioactivity of the fly ash as a consequence of mixing with less radioactive materials. Several researchers have also studied metakaolin for the treatment of heavy metal in industrial waste (Cantarel et al., 2015; Ariffin et al., 2018). However, there are very few studies on the use of natural kaolin geopolymer synthesis for the same purpose. The development of kaolin as a binder has not yet been fully explored and given the substantial deposits of kaolin in Libya this approach to geopolymer production is worthy of further investigation as a means of encapsulating and stabilizing wastes associated with the oil and gas industry.

In this chapter, the ability of natural kaolin and metakaolin to form geopolymers examined in order to solidify and stabilise hazardous drilling waste contaminated soil, and to assess the environmental and technical feasibility of using of these binders as a green and cost-effective binder in waste treatment strategies in the Libyan Desert

climate. The objectives are to use the results of macro and microstructure studies to answer the following questions:

- Could kaolin and meta-kaolin based geopolymers be an efficient way of treating hazardous drilling waste contaminated soils using S/S treatment technology? Is it also possible to use kaolin or metakaolin based geopolymers in a treatment of drilling waste using solidification/stabilisation technique?
- What are the leaching characteristics of the final solidified geopolymer matrices?
- What is the optimum geopolymer composition to immobilise the heavy metals and encapsulate the organic hydrocarbons?

4.2. Materials and Methods

4.2.1 Materials

4.2.1.1 Waste materials

Two samples of soils contaminated with drilling waste were taken from waste pits during drilling of wells for oil production; water-based mud waste (WBM), and oil-based mud waste (OBM) were collected from different pits within Jalu oil field in the Sirte basin. All samples were mixed, prepared and stored as described in Section 2.1.1 in Chapter 2.

The waste contaminated soil samples were used as collected containing all residue chemicals and additives present in the drilling fluids, and products emerging during drilling processes including rock flour. The contamination and toxicity of these drilling waste samples is described in Section 3.1.1 and 3.2.1. Chapter 3. The chemical composition and mineralogy of drilling waste samples was shown in Table 3.1, Chapter 3.

4.2.1.2 Binders

Natural kaolin clay was obtained from the Temenhint area close to the drilling operation. the samples were excavated from the sides of natural slopes and were air dried for 2

weeks, before crushing and sieving through a 1 mm sieve. Metakaolin was prepared by calcination of the kaolin clay at 700 °C for a period of 2 h to produce thermally activated clay with high alumina content as recommended by Kenne Diffo et al., (2015). The chemical composition and crystalline mineralogy of the kaolin, metakaolin are given in Table 4.1.

Table 4.1. Chemical and mineralogical composition of the binders.

Constituent	XRF analysis (wt. %)		
	OPC	Kaolin	Metakaolin
SiO ₂	21.2	47.0	54.0
TiO ₂	0.32	0.00	0.00
Al ₂ O ₃	5.43	39.0	46.0
Fe ₂ O ₃	3.68	0.70	0.78
Mn ₃ O ₄	0.02	0.00	0.00
MgO	1.76	0.14	0.16
CaO	64.5	3.24	3.60
Na ₂ O	0.10	0.40	0.40
K ₂ O	0.73	1.45	1.60
P ₂ O ₅	0.17	0.01	0.00
SO ₃	1.54	0.00	0.00
LOI	1.32	12.3	0.13
XRD Analysis			
OPC	Calcite CaCO ₃ , Calcium silicate Ca ₃ SiO ₅ , Lamite Ca ₂ SiO ₄ , Brownmillerite (Ca ₂ (Al,Fe ⁺³) ₂)		
Kaolin	Kaolinite Al ₂ Si ₂ O ₅ (OH) ₄ , Quart SiO ₂		
Metakaolin	Kaolinite Al ₂ Si ₂ O ₅ (OH) ₄ , Quartz SiO ₂		

4.2.1.3 Additives

Aggregate was sourced from a limestone quarry in the Al-Wahat area close to the drilling operations. Aggregate particles were washed to remove any adherent clay, dried and sieved to obtain material between 2-4 mm in size. Hydrated lime was used to improve the cross-linking within the produced geopolymers and improve the microstructure properties to reduce the efflorescence issue. Both materials were sourced locally.

4.2.1.3 Alkali Activation Solution

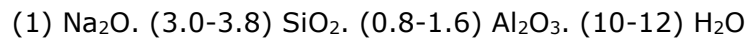
High purity sodium hydroxide (Fisher Scientific UK) was used as the alkali activator in this study. Solutions of NaOH were prepared at concentrations in the range 4-18 M using MilliQ water.

4.2.1.4 Drilling Waste Control Sample

To understand the effect of the presence of petroleum hydrocarbons on geopolymer formation, a sample of WBM was washed to remove all traces of hydrocarbon and then subsequently used alongside the waste contaminated samples. WBM was chosen because it has a similar mineralogy to OBM and lower contamination with organic compounds. This 'control' sample was prepared by shaking 500 g of WBM three times with 2 L of an acetone-hexane solvent mixture to remove any existing hydrocarbons, then the sample was dried at 250 °C to remove any extra solvent or organic materials. This cleaning approach avoids any changes in the mineralogy and texture of the sample.

4.2.2 Geopolymer Recipe Design

In order to obtain high strength and durable geopolymers, technical recommendations on geopolymer chemistry and geopolymer formula proposed by Davidovits, (2011) were followed. This included molar ratios of:



Geopolymer recipes were designed to include quantities of materials as listed in Table 4.2 and selected to obtain geopolymers containing the main oxides with molar ratios close to the formula recommended by Davidovits, (2011), whilst maintaining the overall objective is maximising waste content and minimising the binder, aggregate and chemical additive content in order to create an economically applicable recipe.

Table 4.2: Composition of geopolymer-waste systems (wt. %).

Material	Kaolin –based geopolymer	Metakaolin-based geopolymer
Binder	25	25
Drilling waste (WBM, OBM)	40	40
Aggregate	7-20	7-20
Alkali Activator	4-15	4-15
Lime $\text{Ca}(\text{OH})_2$	10	10
Water	20-30	20-30

Figure 4.1 shows the contributions of metal oxides from each component in the geopolymer recipes. The binder and drilling waste contaminated soil was the main

source of aluminates and silicates, the alkali activator (NaOH) was the primary source of Na^+ needed to balance the charge, and OH^- ions to raise pH allowing breakdown of the aluminosilicate structure needed to begin the geopolymerisation reaction and formation of geopolymer gel, and lime (calcium hydroxide) as a source of CaO to improve setting time, mechanical properties and reduce efflorescence problems.

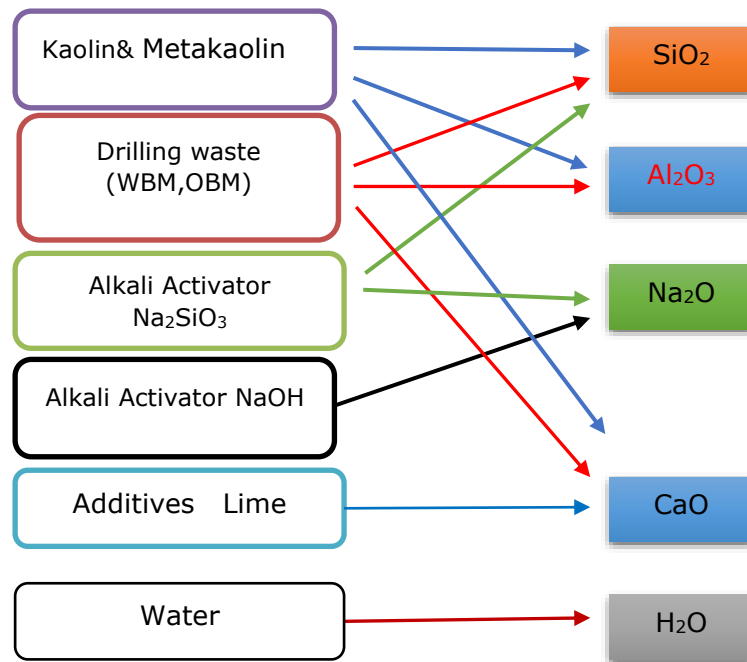


Figure 4.1: Main sources of metal oxides from raw materials in the geopolymer systems.

A total of 30 different geopolymer mixture proportions were prepared using either kaolin or metakaolin binders. Compositions of these mixtures are as given in Table 4.3. The $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio in each treatment was kept as constant as possible. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ (Si/Al) mole ratio shown in table 4.3 represents the total amount of silica in each geopolymer system (including crystalline and amorphous silica). The chemical composition of the mixtures varied by changing the concentration of the alkali activator (NaOH), which changes the overall $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}:\text{SiO}_2$ and $\text{Na}_2\text{O}:\text{CaO}$ molar ratios.

Table 4.3: Recipe mixes and corresponding codes.

Mix	Formula	SiO ₂ :Al ₂ O ₃	Na ₂ O:Al ₂ O ₃	Na ₂ O:SiO ₂	Na ₂ O:CaO	CaO:SiO ₂	H ₂ O:Na ₂ O	NaOH (M)	Water: Solid ratio	TOC. Level wt. %
Kaolin-Control systems										
KC1	1.0 Na ₂ O. 6.2 SiO ₂ . 1.9 Al ₂ O ₃ . 4.8 CaO. 29.3 H ₂ O	3.3	0.5	0.2	0.1	0.7	29.3	3.3	0.3	0.0
KC2	1.0 Na ₂ O. 3.7 SiO ₂ . 1.2 Al ₂ O ₃ . 2.6 CaO. 17.7 H ₂ O	3.3	0.9	0.3	0.2	0.7	17.7	5.8	0.3	0.0
KC3	1.0 Na ₂ O. 2.7 SiO ₂ . 0.8 Al ₂ O ₃ . 1.9 CaO. 12.6 H ₂ O	3.3	1.2	0.4	0.3	0.7	12.6	8.3	0.3	0.0
KC4	1.0 Na ₂ O. 2.1 SiO ₂ . 0.6 Al ₂ O ₃ . 1.5 CaO. 10.0 H ₂ O	3.3	1.6	0.5	0.4	0.7	9.8	10.8	0.3	0.0
KC5	1.0 Na ₂ O. 1.8 SiO ₂ . 0.6 Al ₂ O ₃ . 1.3 CaO. 8.60 H ₂ O	3.3	1.8	0.6	0.5	0.7	8.6	12.5	0.3	0.0
Metakaolin-Control systems										
MKC1	1.0 Na ₂ O. 7.1 SiO ₂ . 2.2 Al ₂ O ₃ . 4.6 CaO. 29.0 H ₂ O	3.2	0.5	0.1	0.2	0.7	28.6	3.3	0.3	0.0
MKC2	1.0 Na ₂ O. 4.3 SiO ₂ . 1.3 Al ₂ O ₃ . 2.8 CaO. 17.5 H ₂ O	3.2	0.7	0.2	0.4	0.7	17.4	5.8	0.3	0.0
MKC3	1.0 Na ₂ O. 3.0 SiO ₂ . 1.2 Al ₂ O ₃ . 2.0 CaO. 12.6 H ₂ O	3.2	1.0	0.3	0.5	0.7	12.5	8.3	0.3	0.0
MKC4	1.0 Na ₂ O. 2.4 SiO ₂ . 0.8 Al ₂ O ₃ . 1.6 CaO. 9.8 H ₂ O	3.2	1.3	0.4	0.6	0.7	9.80	10.8	0.3	0.0
MKC5	1.0 Na ₂ O. 2.1 SiO ₂ . 0.7 Al ₂ O ₃ . 1.4 CaO. 8.5 H ₂ O	3.2	1.5	0.5	0.7	0.7	8.50	12.5	0.3	0.0
Kaolin-WBM systems										
KW1	1.0 Na ₂ O. 6.2 SiO ₂ . 1.9 Al ₂ O ₃ . 6.8 CaO. 29.3 H ₂ O	3.3	0.5	0.2	0.1	1	29.3	3.3	0.3	0.59
KW2	1.0 Na ₂ O. 3.7 SiO ₂ . 1.2 Al ₂ O ₃ . 4.1 CaO. 17.7 H ₂ O	3.3	0.9	0.3	0.2	1	17.7	5.8	0.3	0.59
KW3	1.0 Na ₂ O. 2.7 SiO ₂ . 0.8 Al ₂ O ₃ . 2.9 CaO. 12.6 H ₂ O	3.3	1.2	0.4	0.3	1	12.6	8.3	0.3	0.59
KW4	1.0 Na ₂ O. 2.1 SiO ₂ . 0.6 Al ₂ O ₃ . 2.3 CaO. 9.8 H ₂ O	3.3	1.6	0.5	0.4	1	9.8	10.8	0.3	0.59
KW5	1.0 Na ₂ O. 1.8 SiO ₂ . 0.6 Al ₂ O ₃ . 2.0 CaO. 8.6 H ₂ O	3.3	1.8	0.6	0.5	1	8.6	12.5	0.3	0.59
metakaolin-WBM systems										
MKW1	1.0 Na ₂ O. 6.7 SiO ₂ . 2.2 Al ₂ O ₃ . 6.5 CaO. 29.3 H ₂ O	3.0	0.5	0.1	0.2	1	29.3	3.3	0.3	0.59
MKW2	1.0 Na ₂ O. 4.1 SiO ₂ . 1.3 Al ₂ O ₃ . 3.9 CaO. 17.7 H ₂ O	3.0	0.8	0.2	0.3	1	17.7	5.8	0.3	0.59
MKW3	1.0 Na ₂ O. 2.9 SiO ₂ . 1.0 Al ₂ O ₃ . 2.8 CaO. 12.6 H ₂ O	3.0	1.0	0.3	0.4	1	12.6	8.3	0.3	0.59
MKW4	1.0 Na ₂ O. 2.3 SiO ₂ . 0.74 Al ₂ O ₃ . 2.2 CaO. 9.8 H ₂ O	3.0	1.3	0.4	0.5	1	9.8	10.8	0.3	0.59
MKW5	1.0 Na ₂ O. 2.0 SiO ₂ . 0.65 Al ₂ O ₃ . 1.9 CaO. 8.6 H ₂ O	3.0	1.5	0.5	0.5	1	8.6	12.5	0.3	0.59
Kaolin-OBM systems										
KO1	1.0 Na ₂ O. 7.4 SiO ₂ . 2.1 Al ₂ O ₃ . 7.5 CaO. 19.6 H ₂ O	3.5	0.5	0.1	0.1	1	19.6	5.0	0.2	3.4
KO2	1.0 Na ₂ O. 4.5 SiO ₂ . 1.3 Al ₂ O ₃ . 4.5 CaO. 12.1 H ₂ O	3.5	0.8	0.2	0.2	1	11.8	8.7	0.2	3.4
KO3	1.0 Na ₂ O. 3.2 SiO ₂ . 1.0 Al ₂ O ₃ . 3.2 CaO. 8.4 H ₂ O	3.5	1.1	0.3	0.3	1	8.4	12.5	0.2	3.4
KO4	1.0 Na ₂ O. 2.5 SiO ₂ . 0.7 Al ₂ O ₃ . 2.5 CaO. 6.6 H ₂ O	3.5	1.4	0.4	0.4	1	6.6	16.2	0.2	3.4
KO5	1.0 Na ₂ O. 2.2 SiO ₂ . 0.6 Al ₂ O ₃ . 2.2 CaO. 5.7 H ₂ O	3.5	1.6	0.5	0.5	1	5.7	18.7	0.2	3.4
Metakaolin-OBM systems										
MKO1	1.0 Na ₂ O. 7.9 SiO ₂ . 2.4 Al ₂ O ₃ . 7.5 CaO. 19.6 H ₂ O	3.0	0.5	0.2	0.1	1	19.6	5.0	0.2	3.4
MKO2	1.0 Na ₂ O. 4.8 SiO ₂ . 1.5 Al ₂ O ₃ . 4.5 CaO. 12.1 H ₂ O	3.0	0.8	0.3	0.2	1	11.8	8.7	0.2	3.4
MKO3	1.0 Na ₂ O. 3.4 SiO ₂ . 1.0 Al ₂ O ₃ . 3.2 CaO. 8.4 H ₂ O	3.0	1.1	0.3	0.4	1	8.4	12.5	0.2	3.4
MKO4	1.0 Na ₂ O. 2.7 SiO ₂ . 0.8 Al ₂ O ₃ . 2.5 CaO. 6.6 H ₂ O	3.0	1.4	0.4	0.5	1	6.6	16.2	0.2	3.4
MKO5	1.0 Na ₂ O. 2.2 SiO ₂ . 0.7 Al ₂ O ₃ . 2.5 CaO. 5.7 H ₂ O	3.0	1.5	0.5	0.6	1	5.7	18.7	0.2	3.4

4.2.3 Mixing Process

Geopolymer mortar mixes were prepared using proportions of raw materials as given in Table 4.3. The dry materials were blended using a Kenwood mixer at 140 rpm for 10 minutes to ensure homogeneity. The alkali activator solution was prepared and left to cool to room temperature for 24 h. The water: solid ratio was kept constant for each binder-waste system; 0.3 for KW and MKW mixtures and 0.2 for KO and MKO mixtures. The activating solution was introduced slowly into the dry materials during the mixing until a homogeneous mixture was obtained before the aggregate material was added to the paste.

4.2.4 Casting Process

After mixing the materials and preparation of the mortars, three different moulds were used to prepare sample specimens. The majority of the fresh geopolymer mixture was cast into cylindrical moulds (100 mm long x 50 mm diameter) for UVP and UCS tests. A separate portion of the freshly prepared geopolymer was poured into polystyrene moulds (c.10 cm³ volume) to cast samples for testing of apparent density, water absorption percentage and total void volume. A final portion was cast into cuboid shaped polystyrene dishes (10 mm deep x 35 mm length and width) to obtain samples for FTIR and XRD analysis and for measuring degree of reaction, total leachability and leachate material concentration. Once poured, all moulds were gently shaken for 5 minutes to encourage settling and removal of air traps and voids before curing.

4.2.5 Curing condition

Samples were cured in a programmable incubator with a temperature regime designed to simulate changes in temperature during the summer period in the Jalu area of the Libyan Desert as shown in Table 4.4.

Table 4.4: Programmed daily temperature regime for Jalu, Libyan Desert during July. Temperature Simulation, Jalu (July).

Time	5 am	8 am	11 am	2 pm	5 pm	8 pm	11 pm	2 am
Temperature (°C)	26	29	34	38	39	34	31	28

All samples and subsamples were cured using the temperature cycle and at a relative humidity varying between 50-80% for 24 hours, before demoulding. Samples were then placed back into the incubator and allowed to continue curing for a further 28 days until testing.

4.2.6 Testing of samples

4.2.6 1 Physical analysis (macroscopic properties)

To predict the durability of the geopolymers and cement-based equivalents, a range of physical tests were undertaken. A water absorption test was conducted according to British Standard testing method BS EN 772-11 as described in Section 2.2.2, Chapter 2, a bulk density test according to British Standard BS EN12390-7 as described in Section 2.2.3, Chapter 2, the percentage of total pore volume was determined to measure the porosity accessible to water using standard testing method ASTM C642 as described in Section 2.2.4, Chapter 2.

4.2.6.2 Chemical analysis:

The composition of powdered raw materials (metal oxide form) was determined by X-ray fluorescence (Axios Advanced) as described in section 2.2.11, Chapter 2, and elemental composition was measured by ICP-MS type iCAP-Q (Thermo Scientific) after digestion of the material (see Section 2.2.11, Chapter 2).

The acid attack method described in section 2.2.1, Chapter 2 was used to:

- Monitor and evaluate the degree of geopolymerisation reaction in control geopolymers KC, MKC, K-waste geopolymers (KW, KO) and MK-waste geopolymers (MKW, MKO)
- Study the effect of petroleum hydrocarbon contamination on the degree of geopolymerisation in all formulated geopolymers

The leachability behaviour of all formulated geopolymers was evaluated using ICP-MS for measurement of heavy and toxic metals and GC-FID for measuring of petroleum hydrocarbons in leachate as described in Sections 2.2.7, 2.2.8 and 2.2.9, Chapter 2.

4.2.6.3 Microstructural changes

To evaluate the changes in mineralogy and formation of new chemical bonds FT-IR measurements were performed using an Infrared spectrophotometer type Bruker 27 TENSOR Series instrument as described in section 2.2.13, Chapter 2, X-ray diffraction (XRD) patterns were measured using a Hilton brooks PW1050 X-ray diffractometer to check mineralogy and phase transformation of raw materials and hardened geopolymers as described in Section 2.2.12 in Chapter 2.

4.3 Results and discussions

4.3.1 Geopolymemisation of kaolin, metakaolin-waste systems and effect of alkali activator dosage

The transformation of drilling waste control sample to solid matrixes through geopolymerisation reaction using kaolin and metakaolin as binders and sodium hydroxide as alkali activator was studied by conducting several experiments. Firstly, to investigate the ability of raw materials to transform to geopolymer gel, and secondly to select the appropriate alkali activator dosage needed for dissolution of raw materials avoiding using of extra dosages leads to formation of geopolymers with poor internal structure with efflorescence problems.

In these experiments, the performance of control geopolymer systems (KC and MKC systems) illustrated in table 4.3 containing almost (0 wt.% TOC) was evaluated by measuring the degree of alkali activation reaction and measure the quantity of gel formed. The degree of geopolymerisation reaction was evaluated using acid attack test proposed by Fernández-Jiménez et al., (2006) as described in section 2.2.1, Chapter 2. In this test, the acid reacts with all alkali activation reaction products (NASH, CSH,

CASH) dissolve it completely, while the unreacted silicates or aluminates in starting material (kaolin, metakaolin, drilling waste control) remained unaffected.

Figure 4.2 shows that all proposed geopolymer control recipes (KC and MKC) successfully produce aluminosilicate gel and transformed into a solid matrix to varying degrees due the effect of alkali activator concentration.

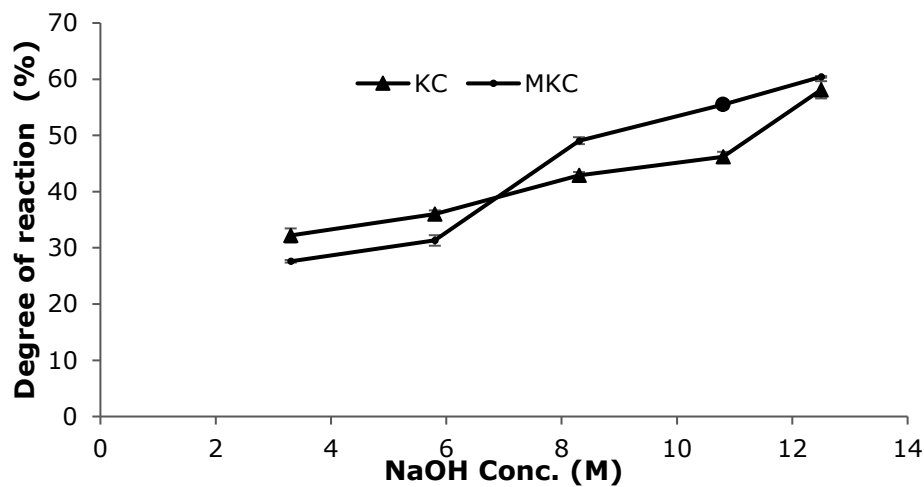


Figure 4.2: Effect of alkali activator (NaOH) dosage in improvement of formation of geopolymer gel. The figure shows the effect of Alkali activator (NaOH) dosage in enhancement of formation of geopolymer gel in kaolin and metakaolin control geopolymer systems. Error bars indicate the standard deviation of five data points in triplicate.

The results shown in Figure 4.2 indicate that the amount of unreacted materials was high, and the degree of geopolymerisation and formation of geopolymer gel in both systems was poor at lower NaOH concentrations. The formation of geopolymer gel increased with increasing concentration of NaOH solution between (5.8 -12.5M). The highest degree of geopolymerisation in both systems was achieved using greater concentrations of NaOH solution (~ 12.5 M).

During the preparation of geopolymers it was noticed that higher concentration of NaOH (10.8 -12.5 M) produced a very viscous geopolymer mixture which results in compaction problems and reduces the workability and flow of the geopolymer paste.

The influence of NaOH solution concentration in enhancing the formation of geopolymer gel is in line with the observations of previous studies conducted by Kathirvel et al., (2014) and Pangdaeng et al., (2018) who concluded that higher alkali activator concentrations increased the dissolution of the initial solid materials, and reflects positively on the degree of formation of geopolymer gel.

The results obtained from KC and MKC systems indicates that there was a significant variation in the degree of reaction for both systems at the p-value < 0.001 level. MKC geopolymers showed greater formation of geopolymer gel which may correlated with the difference in $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of both systems (~3.3 KC and 3.2 MKC systems), attributed to the higher content of aluminium oxide in MKC systems which promotes the geopolymerisation reaction. Tchakoute et al., (2012) reached a similar conclusion.

4.3.2 Geopolymerisation of drilling waste and effect of petroleum hydrocarbons

Several recipes K-waste & MK-waste based geopolymers (KW, MKW contain 0.56 wt.% TOC) and (KO, MKO contain 3.4 wt. % TOC) illustrated in Table 4.3 were prepared by keeping the quantity of all materials constant (binder, additives and drilling waste), adding the same quantity of hydrated lime, and changing only the alkali activator concentration and quantity of water in KO and MKO systems. The recipes were formulated to comply with the optimum metkaolinite geopolymer formula that achieved the highest performance as suggested by Roweles et al., (2003), Kamalloo et al., (2010), and Davidovits, (2011).

(3.0-3.8) $\text{SiO}_2/\text{Al}_2\text{O}_3$, (1-1.6) $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and (10-12) $\text{H}_2\text{O}/\text{Na}_2\text{O}$.

To compare the degree of transformation of drilling waste to geopolymer gel in all proposed binder-waste recipes, the acid attack test was followed again. Figure 4.3 shows the effect of changing the formulations listed in Table 4.3 on the degree of geopolymerisation of KW, MKW, KO and MKO mixes.

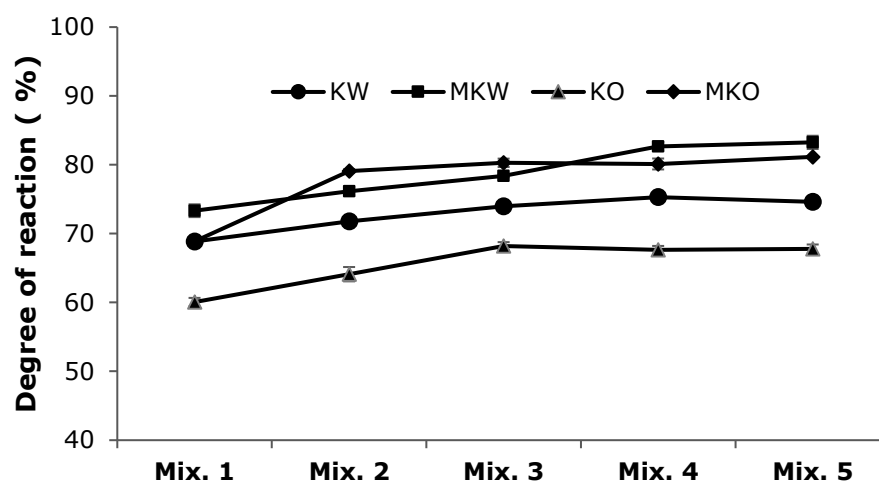


Figure 4.3: Comparison of the degree of geopolymerisation reaction for KW, MKW, KO and MKO systems as a function of increasing NaOH concentration.

The Figure shows the effect of formulation and the effect of existence of TPH in transformation of kaolin, metakaolin -waste to geopolymer gel. The error bars indicate the standard deviation of five data points in triplicate.

The results also confirm the effect of lower $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio in MK recipes in formation of more alkali activation products within MK-waste systems comparing with K- waste systems.

The results show that the maximum quantity of gel formed in KW, KO, MKO was achieved by Mix. 3 (KW3, KO3 and MKO3) and recipe Mix. 4 (MKW4) in MKW system. The results indicate that all mixes successfully produced aluminosilicate gel with the maximum geopolymer gel formation using alkali activator concentration (8.3 M) for KW3, (12.5 M) for KO3 and MKO3 systems and (10.8 M) for MKW4 systems. As figure 4.3 shows, there is a significant difference resulted from changing alkali activator solution concentration in all systems (p -value < 0.001 in KW, MKW and MKO systems and < 0.03 in KO system).

The results strengthen the suggestion of many researchers and authors in geopolymer chemistry about the optimum geopolymer formula to achieve the highest

geopolymerisation degree and performance. The recipes which was produced the maximum alkali activation products (geopolymer gel and other gels) in this study was:

Recipe KW3: (3.3) $\text{SiO}_2/\text{Al}_2\text{O}_3$, (1.2) $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and (12.6) $\text{H}_2\text{O}/\text{Na}_2\text{O}$.

Recipe MKW4: (3.0) $\text{SiO}_2/\text{Al}_2\text{O}_3$, (1.3) $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and (9.8) $\text{H}_2\text{O}/\text{Na}_2\text{O}$.

Recipe KO3: (3.5) $\text{SiO}_2/\text{Al}_2\text{O}_3$, (1.1) $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and (8.4) $\text{H}_2\text{O}/\text{Na}_2\text{O}$.

Recipe MKO3: (3.0) $\text{SiO}_2/\text{Al}_2\text{O}_3$, (1.1) $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and (8.4) $\text{H}_2\text{O}/\text{Na}_2\text{O}$.

The lower $\text{H}_2\text{O}:\text{Na}_2\text{O}$ molar ratio in KO3 and MKO3 explained by the hydrophobic nature of petroleum hydrocarbon in these recipes which led to usage of lower water volume to achieve the best workability and mixing condition.

For better understanding of the effect of petroleum hydrocarbon content in drilling waste on the degree of geopolymerisation reaction for each system, the degree of reaction for recipe 3 was compared for control, kaolin-waste and metakaolin-waste systems (KC3, KW3, KO3, MKC3, MKW3 and MKO3). The selected recipes have almost identical chemical composition and texture but contain different concentrations of petroleum hydrocarbons. The results clearly showed a negative effect of petroleum hydrocarbon content and a significant decrease (p -value < 0.001) in formation of geopolymer gel in kaolin or metakaolin-waste systems contain higher TPH concentrations. The results also suggest that petroleum hydrocarbon contents below (0.59 wt.% TOC approx. 5600 mg kg^{-1}) had no effect on the degree of geopolymerisation reaction and formation of geopolymer gel, but TPH concentrations of (3.4 wt. % TOC approx. 34000 mg kg^{-1}) reduce the formation of geopolymer gel by approx. 20 % when compared to the control (Figure 4.4).

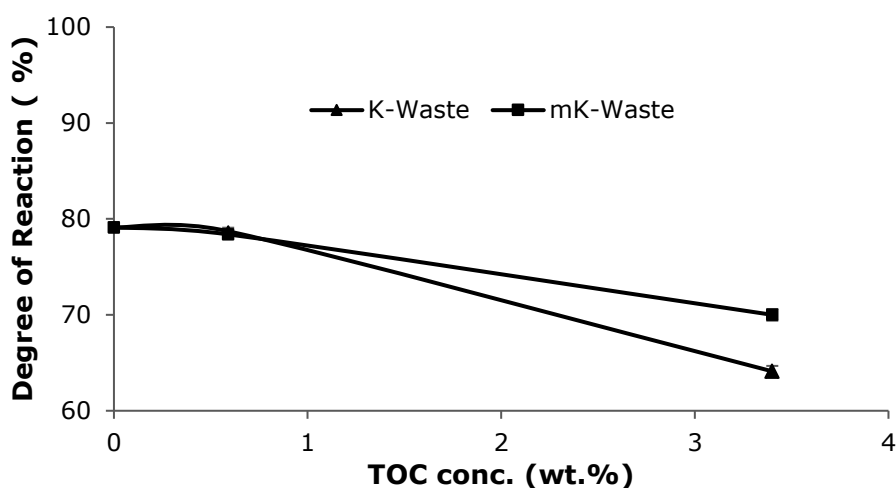


Figure 4.4: Effect of TOC conc. on reduction of formation of geopolymer gel in KW and MKO systems. The Figure shows the negative effect of the high concentration of petroleum hydrocarbons on the degree of geopolymerisation reaction and formation of geopolymer gel. The error bars represent the standard deviation of the mean of 3 data points in triplicate for each system.

4.3.3 Effect of changes in geopolymer formulation on degree of geopolymerisation and microstructure changes in K-waste geopolymer systems

FT-IR and XRD analysis for KC, KW, and KO recipes listed in Table 4.3 was conducted for the purposes of comparison and to examine microstructural changes conjugated with the transformation of raw materials to geopolymer gel in KW and KO geopolymer systems, and investigate the microstructure changes resulted from the addition of lime to those systems.

In general, the FTIR spectra obtained from those systems contain bands at approximately 1025 cm^{-1} which assigned for typical Si-O vibrations and considered as indication of the excitation of quartz as reported by Tchakoute et al., (2013) and Guzmán et al., (2017). There are also major bands at approximately 3600, 1640, 1410, 910, 870, and 780 cm^{-1} . Bands at 3600 and 1640 cm^{-1} are typical of the O-H stretching and the H-O-H bending vibration respectively, and used as indication of existence of hydroxyl groups resulting from either the alkali activator (NaOH) or water. The band at 1440 cm^{-1} is assigned to carbonate compounds. Bands at 870 and 910 cm^{-1} are assigned to the stretching of the Si-O and Al-O groups and the band around 789 cm^{-1} is indicative of the vibration of Al-O or Si-O-Al groups.

Formation of geopolymers is indicated in FTIR spectra by the broad, intense X-O band (X=Si or Al) located in the 950–1000 cm^{-1} range attributed to the Si-O-Si and Si-O-Al vibrations, representing the combination of both Al-O and Si-O and reflecting the extent and magnitude of the incorporation of aluminates and silicates in gel formation. This important peak is attributed to the amorphous nature of the geopolymer gel and indicative of short-range order of Si and Al tetrahedral (Elimbi et al., 2011; Tome et al., 2018). The band is considered a fingerprint of geopolymer matrices and used as evidence to prove the formation of sodium aluminosilicate hydrated gel (NSAH).

Figure 4.5 compares FTIR results obtained from kaolin control geopolymer activated using only NaOH (KC3) and geopolymer system activated using NaOH in presence of hydrated lime (KW3). The main difference between the KC3 and KW3 spectra is the band at 950-1000 cm^{-1} (Figure 4.5). the spectra shown that the magnitude in conversion of raw materials to geopolymer gel identified by formation of Si-O-Si or Si-O-Al at FTIR band between 950-1000 cm^{-1} was higher in KW systems.

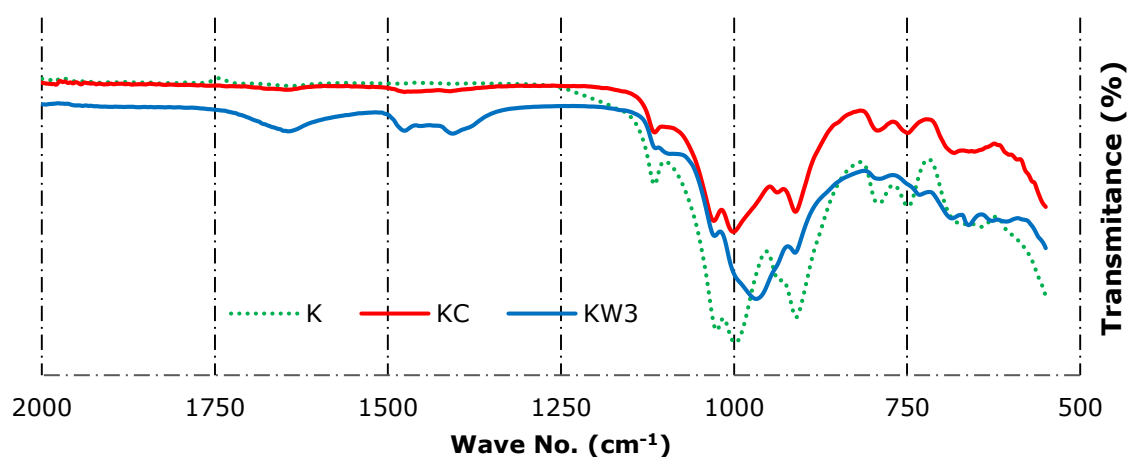


Figure 4.5: Effect of addition of lime in enhancement of transformation of KW system to geopolymers.

The FTIR band between 950–1000 cm^{-1} indicate the extent of transformation of aluminosilicate materials to geopolymer gel and formation of Si-O-Si and Si-O-Al bonds in each system. The Figure also illustrates the positive effect of adding lime in recipe KW3 on the enhancement of geopolymer gel formation comparing to KC recipe activated using NaOH only and raw Kaolin binder

This indicates that the addition of lime is beneficial in increasing the conversion of raw materials to geopolymer gel or any other alkali activation products such as CSH. This finding is fully compatible with the previous observations on the degree of geopolymerisation in systems containing lime, and fully agree with other studies that concluded the positive effect of addition of lime in transformation of aluminosilicate materials to geopolymers (Abdel-Gawwad and Abo-El-Enein, 2016; Hake et al., 2018). The effect of addition of lime on enhancement of production of alkali activation products may be explained by the fact that lime works as an alkaline medium improving the dissolution of the aluminosilicate materials helping to convert the aluminosilicate materials to hydrated sodium aluminosilicate NASH gel, and also lime provides Ca^{+2} ions which promote the production of calcium silicate hydrate CSH gel and/or calcium silicate aluminate hydrate CASH gel as concluded by Temuujin et al., (2009) and Criado et al., (2016) in similar work.

For more understanding to the effect of petroleum hydrocarbons concentration on the geopolymerisation reaction and gel formation extent in KW and KO system, recipes KW3 containing 0.59 wt. % TOC, and KO3 containing 3.4 wt. % TOC exhibited higher degree of gel formation in each system were selected to investigate the effect of organic hydrocarbon contamination level in geopolymerisation process. The FTIR spectra in figure 4.6 show that the intensity of the peak between $950\text{--}1000\text{ cm}^{-1}$ in KW systems is sharper and higher in the magnitude comparing with the peak obtained by KO3 system. This result indicates that the conversion of raw aluminosilicate materials in Kaolin-WBM (KW3) systems to geopolymer gel was higher than the conversion in kaolin-OBMW (KO3) system and confirms the destructive effect of higher TPH concentrations. This result is consistent with the observation emerged by measuring the degree of geopolymerisation in KW and KO systems explained in section 4.6.2 and figure 4.3.

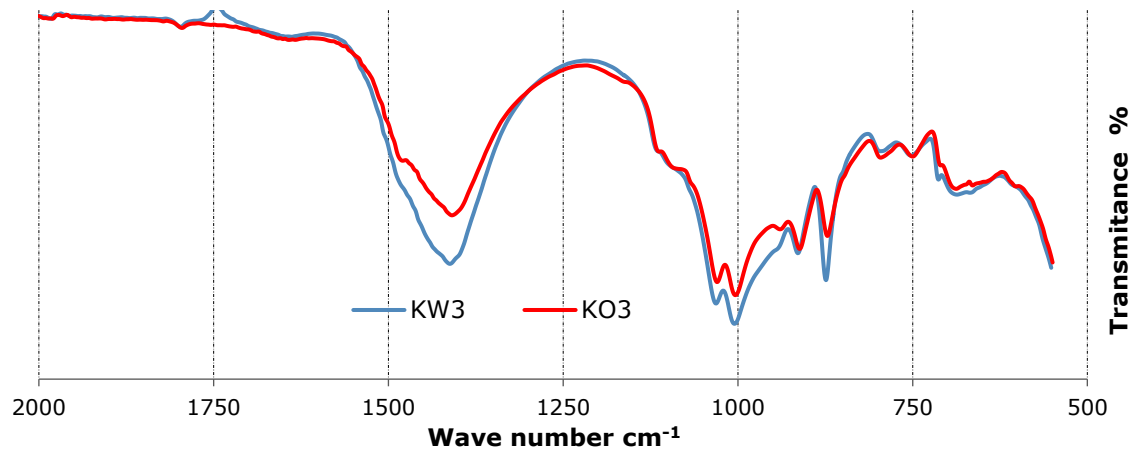


Figure 4.6: Effect of TPH concentration on formation of geopolymer gel in K-waste systems. The figure indicates lower degree of geopolymerisation in KO3 system contain higher TPH concentrations (indicated by the peak between 950-1000 cm^{-1}), comparing with KW3 system.

The results in Figure 4.7 illustrate the effect of concentration the alkali activator concentration across the KW geopolymer formulations. The results confirm the findings of section 4.6.2 regarding selection of recipes KW3 as optimum recipe in KW system exhibited the higher degree of geopolymerisation and formation of geopolymer gel. The higher magnitude of conversion of raw kaolin and WBM waste in recipe KW3 to geopolymer gel may attributed to the recipe formulation and applying of the appropriate alkali activator concentration which was designed to comply with the optimum kaolinite geopolymer formula that achieved the highest performance as concluded in many previous studies (Roweles et al., (2003); Davidovits, (2011)).

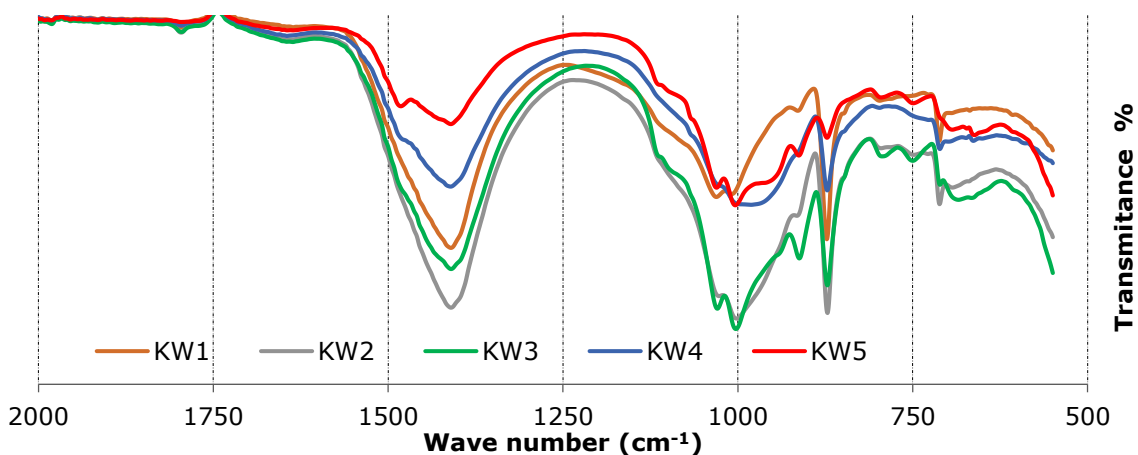


Figure 4.7: FTIR Spectra showing structural changes in KW geopolymers prepared using different formulation by changing the alkali activator concentration (NaOH).

The Figure showed that KW3 activated by 8.3M NaOH have exhibited the highest magnitude of conversion to geopolymer gel as indicated by the intense IR band at wave number 1000 cm^{-1} .

Figure 4.8 shows the destructive effect of high concentration of petroleum hydrocarbons in K-OBM system by reduction conversion of raw materials to geopolymer gel. The same figure also indicates that recipes (KO3, KO4 and KO5) shows the maximum transformation of kaolin-waste to geopolymer gel in this system.

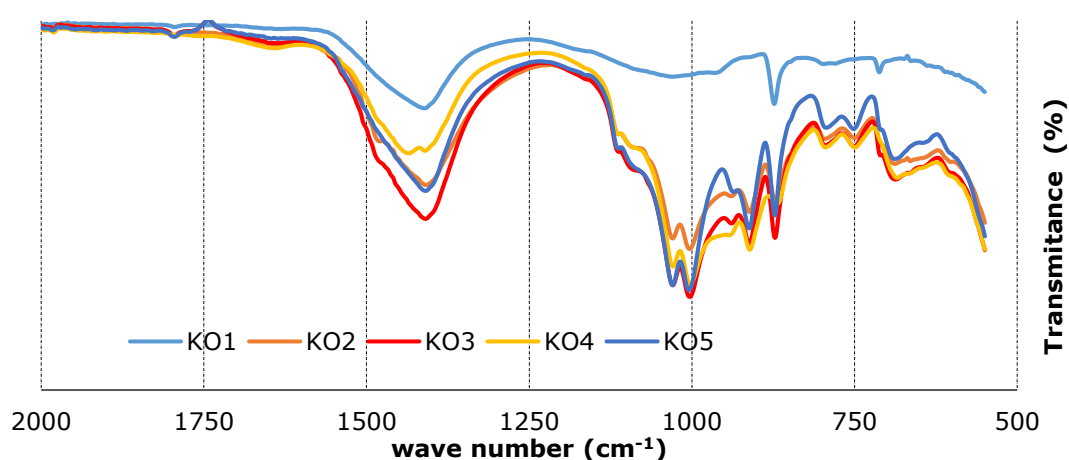


Figure 4.8: FTIR Spectra showing structural changes in KO geopolymers prepared using different formulation by changing the alkali activator concentration (NaOH). The figure showed that KO3, KO4 and KO5 activated by 12.5M, 16.2M and 18.7M NaOH respectively have exhibited the greatest magnitude of conversion to geopolymer gel as indicated by the intense IR band at wave number 1000 cm^{-1} .

As previously concluded, the higher concentration of petroleum hydrocarbons in OBM has destructive effect in the transformation of raw aluminosilicate materials within the waste to geopolymer gel in KO systems.

In order to investigate the main mineralogy changes accompanied the transformation of raw materials (kaolin and WBM) to geopolymers, X-ray diffraction analysis was conducted for raw materials kaolin, WBM and for KW3 recipe exhibited the higher degree of formation of geopolymer gel in KW geopolymer system. The X-ray analysis

included KW3 system activated only by NaOH, and KW3 system activated by NaOH in existence of lime.

The mineralogy analysis in raw materials Kaolin and WBM illustrated as shown in Table 4.1 shows that the drilling waste sample WBM contains a high percentage of Calcite CaCO_3 , quartz SiO_2 and Ankerite $\text{Ca}(\text{Fe}^{+2}\text{Mg})(\text{CO}_3)_2$, where the Kaolin contains Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and Quartz SiO_2 as major minerals. The below diffractogram (Figure 4.9a) show the X-ray analysis for kaolin binder, figure 4.9.b Kaolin-WBM geopolymer system KW3 activated only by NaOH and hardened for 28 days, where figure 4.9.b shows the X-ray diffraction patterns obtained from Kaolin-WBM geopolymer system KW3 activated by NaOH in the existence of lime and hardened for the same period. By comparing the X-ray diffractograms for the geopolymer matrices (Figure 4.9.a, b and c), It is clearly to observe that most of the mineral phases in raw materials were transformed to other phases with different chemical composition and structure, which confirm that the alkali activation reaction was take place in those systems and formation of new products, and that the aluminosilicate precursors within the raw material were reorganised to form geopolymer gel phases and zeolites phases.

Significant difference can be observed between the quantity and the quality of the newly formed geopolymer matrices using and it depends of the type of alkali activator used. It can be seen that the activation of KW system using only NaOH was not sufficient to transform all aluminium silicate materials present in the KW system to aluminosilicate gel, and there is a quantity of unreacted kaolinite initially introduced by Kaolin binder, or calcite and quartz introduced by WBM still remaining within the KW geopolymer matrices.

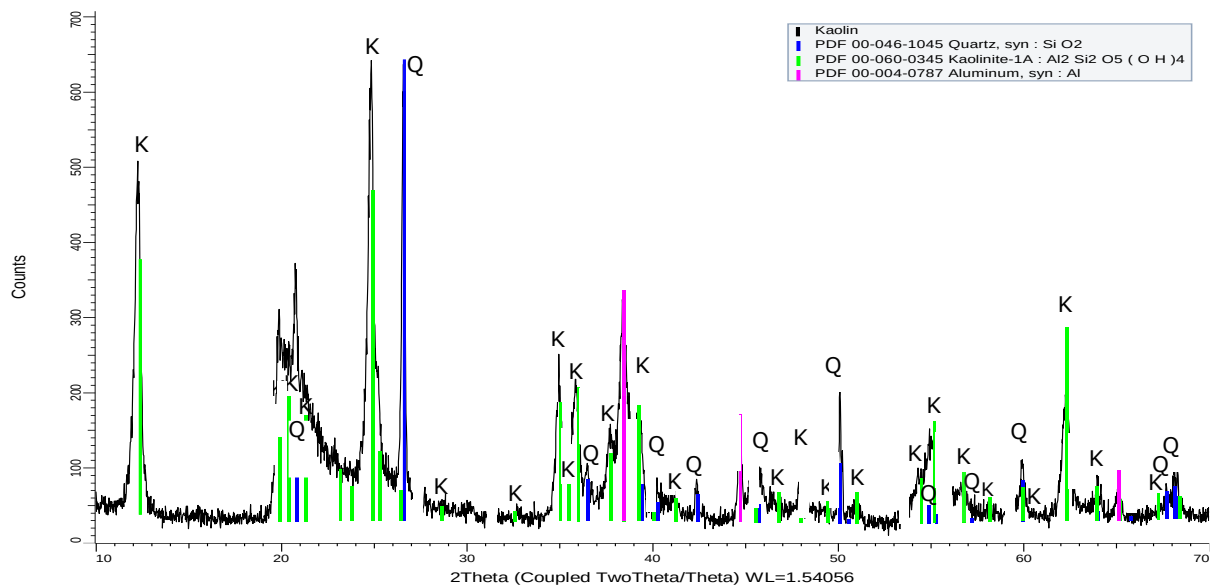


Figure 4.9a. X-ray diffraction patterns obtained from kaolin binder

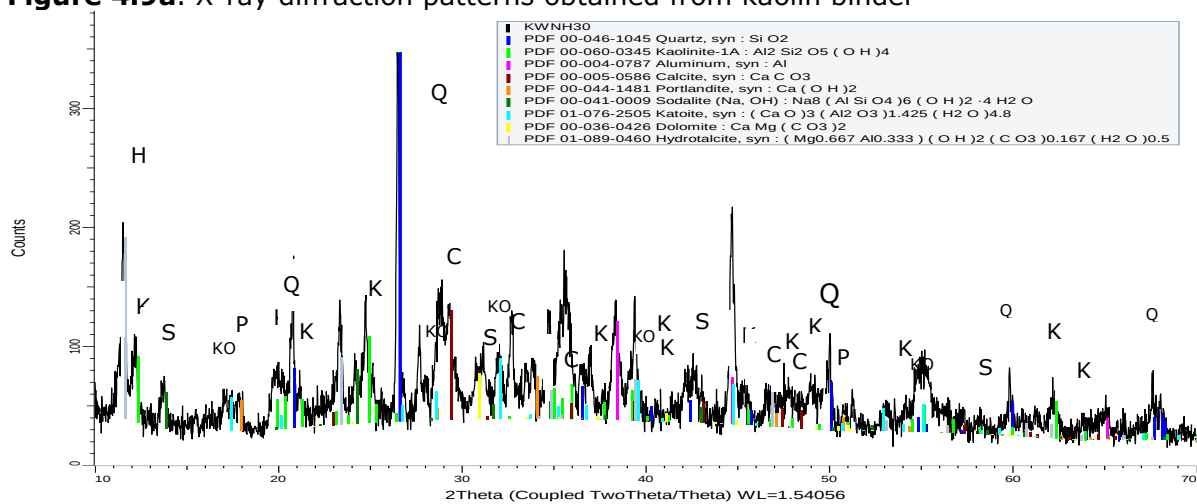


Figure 4.9b. X-ray diffraction obtained from KW geopolymer activated only by NaOH

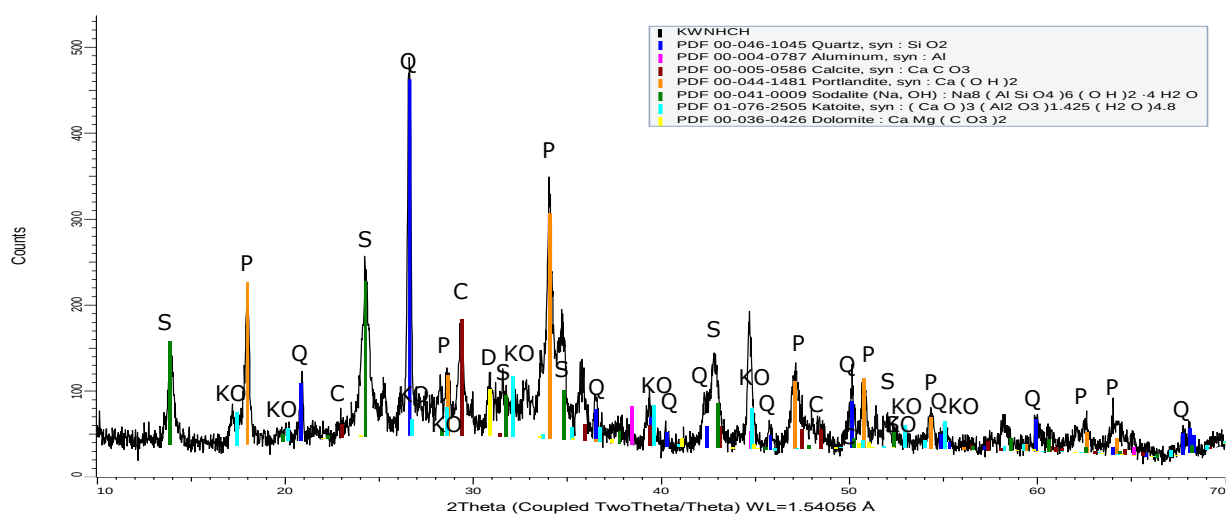


Figure 4.9c. X-ray diffraction patterns obtained from KW geopolymer activated only by NaOH and lime.

Figure 4.9a represent the phases exist in kaolin binder before activation, figure 4.9b represent the phases obtained by geopolymerisation of KW systems using only NaOH as alkali activator. X-ray diffractogram indicate formation of new phases such as sodalite (S), Katoite (KO), Hydrotalcites (H) and dolomite (D) and the existence of quartz (Q), calcite (C) and kaolinite (K) phases remaining unreacted from Kaolin or WBM raw materials.

Figure 4.9c, shows the X-ray diffractogram for the same recipe (KW3) activated by NaOH in presence of lime (Ca(OH)_2). The Figure shows that all kaolinite phase introduced by kaolin binder in the system was completely consumed and transformed to other phases, where quantities of quartz and calcite still remaining unreacted. The XRD diffractograms for the remaining materials in KW system included in appendix 2.

The same XRD diffractograms (Figure 4.9b and 4.9c) indicate that the newly produced phases vary in its composition and structure. The most important produced phase within KW geopolymer systems was hydrosodalite $(\text{Na,OH}): \text{Na}_8(\text{AlSiO}_4)_6 (\text{OH})_2 \cdot 4\text{H}_2\text{O}$ composed mainly from $(\text{Na}, \text{Al}_2\text{O}_3, \text{SiO}_2 \text{ and } \text{H}_2\text{O})$, and Katoite $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_1.5(\text{OH})_6$ composed from $(\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2 \text{ and } \text{H}_2\text{O})$, and hydrotalcite $(\text{Mg}_{0.667}\text{Al}_{0.333})(\text{OH})_2(\text{CO}_3)_{0.167}(\text{H}_2\text{O})_{0.5}$ composed from $(\text{Mg}, \text{Al}, \text{CO}_3 \text{ and } \text{H}_2\text{O})$ (Barthelemy, 2019).

As concluded in the previous tests regarding the positive effect of adding lime, the results obtained from XRD analysis of KW systems activated by NaOH in the existence of lime confirms the significance in the transformation of Kaolinite phase existence in Kaolin binder to two new phases only, hydrosodalite phase with chemical formula $(\text{Na,OH}): \text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and Katoite phase with chemical formula $(\text{CaO})_3(\text{Al}_2\text{O}_3)_{1.425}(\text{H}_2\text{O})_{4.8}$. which may use as prove for formation of NSAH and CAH phases within this system.

As mentioned in the literature, the presence of hydrosodalite peak reveals formation of a Kaolinite/Hydrosodalite-based geopolymer composed from poly(sialate) molecular unit with $\text{Si}_2\text{O}:\text{Al}_2\text{O}_3$ mole ratio ($=2$) (Davidovits, 2008; Markovska, 2009), and that Hydrosodalite have amorphous microstructure of zeolite (El-Eswed et al.,2015; Marsh et al.,2018).

A number of authors have studied the characterisation and microstructure of hydrosodalite and found that hydrosodalite is the only member of the sodalite family with zeolitic properties (Buhl, 2017). The results reveal that the geopolymerisation reaction between Na_2O , SiO_2 , and Al_2O_3 takes place as a result of alkali activation of kaolinite phase to form kaolin/zeolite based geopolymers. with amorphous to semi-crystalline polymeric structures as shown in Figure 4.10 as described Baerlocher et al, (2007). The hydrosodalite framework illustrated in the same Figure by Som web., (2019), as SiO_4 (blue) and AlO_4 (green) tetrahedral surrounding cages containing sodium ions (yellow) and anion sites (pink).

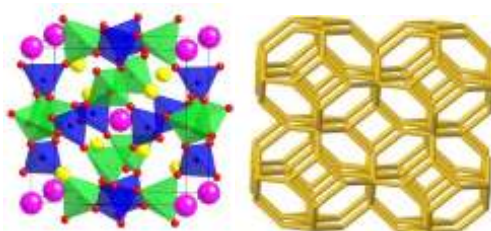


Figure 4.10: Hydrosodalite framework (Na-P) as Baerlocher et al. (2007), and Som web, (2019).

The formation of kaolin/zeolite based geopolymers take advantage of both constituents: high surface area, pore volume and adsorption capacity from zeolites, and strength and support from geopolymer matrix as reported by Rožek and Mozgawa, (2019). Several studies indicate that hydrosodalite characterized by a denser lattice, higher stability and high specific surface area allows for good sorption capacity (Yu et al. 2014; Davidovits, 2015). The application of hydrosodalite as reported by Moshoeshoe et al., (2017) comprise different areas of industry inclusive of technology and environmental remediation such as pollution control and disposal of hazardous materials.

The second new phase formed within the KW geopolymer system was katoite, also known in the literature by hydrogarnet, which is type of calcium-based geopolymer composed from (Ca, K, Na)-sialate molecular unit with $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio (2,4 or 6) (Davidovits, 2008).

Calcium aluminatesilicate phase formed in the geopolymers when amounts of Al^{+3} ions reacts with the calcium ions Ca^{+2} as reported by Pangdaeng et al., (2018).

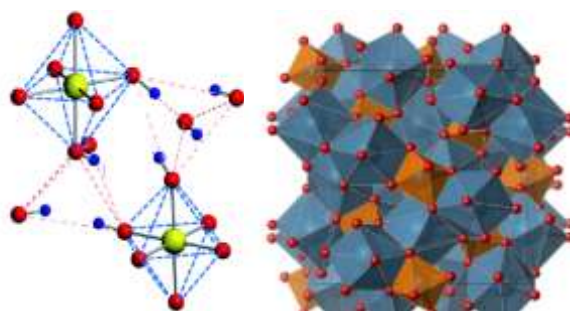


Figure 4.11: Katoite framework. Erba et al., (2015): (Crystal symmetry. (2019).

The katoite phase have the chemical structure shown in Figure 4.11 as suggested by Erba et al., (2015) (oxygen atoms in red, silicon in green, aluminium in yellow, hydrogens in blue), and have the framework shown in same Figure where the blue cubes represent the CaO_8 and the orange octahedra present AlO_6 (Crystal symmetry. 2019). Also, Katoite compounds found useful for different environmental applications due to its higher organic compounds adsorbent capacity as reported by Maeda et al., (2019).

The third new formed phase was Hydrotalcites (HTs), with structure framework showed in Figure 4.12, which have chemical formula $(\text{Mg}_{0.667}\text{Al}_{0.333})(\text{OH})_2(\text{CO}_3)_{0.167}(\text{H}_2\text{O})_{0.5}$ and have the framework structure illustrated by Perotti et al., (2014) contains typical layered double-metal hydroxides structure shown in Figure 4.12.

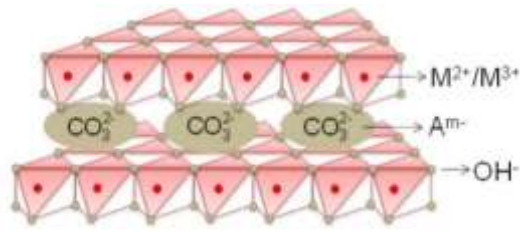


Figure 4.12: Hydrotalcites framework (Perotti et al. 2014)

Hydrotalcites have unique characteristics qualify it for use in different environmental applications such as cation-exchange ability, anion-exchange ability, surface adsorption capacity, surface basicity as reported by many researches (Parker et al., 1995; Perotti et al. 2014; Shekoohi et al., 2017).

The XRD patterns of KO geopolymer sample are shown in Figure 4.13, after the geopolymerisation process, a number of characteristic peaks in the XRD diffractograms indicate remaining of part from raw materials unreacted in KO geopolymer system. The remaining materials present the phases introduced from the raw material such as quartz, barite and calcite from OBM, and kaolinite from kaolin binder which indicate incomplete alkali activation reaction. The new peaks appeared on the XRD patterns of KO geopolymer sample hydrosodalite and katoite formed as result of geopolymerisation reaction, and portlandite present the remaining lime (Ruiz and Cuevas, 2014), and dolomite (calcium magnesium carbonate $CaMg(CO_3)_2$) which formed based on the interaction between lime and calcite materials in high alkaline condition as reported by Banerjee, (2016).

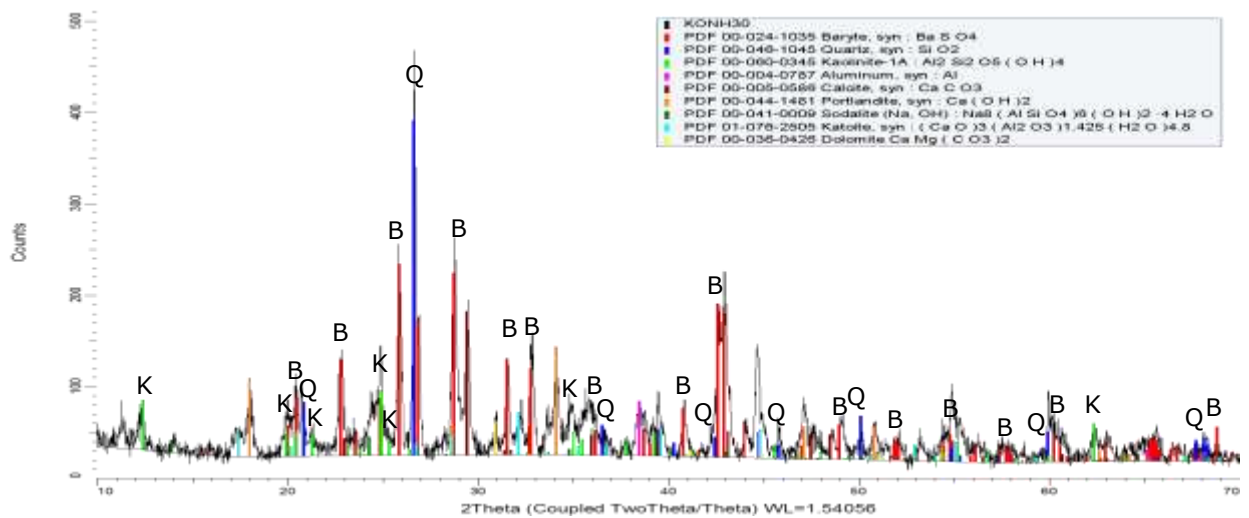


Figure 4.13: X-ray diffraction patterns of KO geopolymers

4.6.4 The effect of formulation on the degree of geopolymerisation and microstructure changes in MK-waste geopolymer systems

The results illustrated in the FTIR spectra (Figure 4.14 for MKW, Figure 4.15 for MKO system) shows the degree of the transformation of raw materials in MK-waste systems. Both systems exhibit low ability to transform to geopolymer materials when compared with results obtained by KW and KO systems. The most remarkable observations were the lower extent of alkali activation products formed in MK-waste systems comparing with K-waste systems despite the higher aluminates content on metakaolin binder.

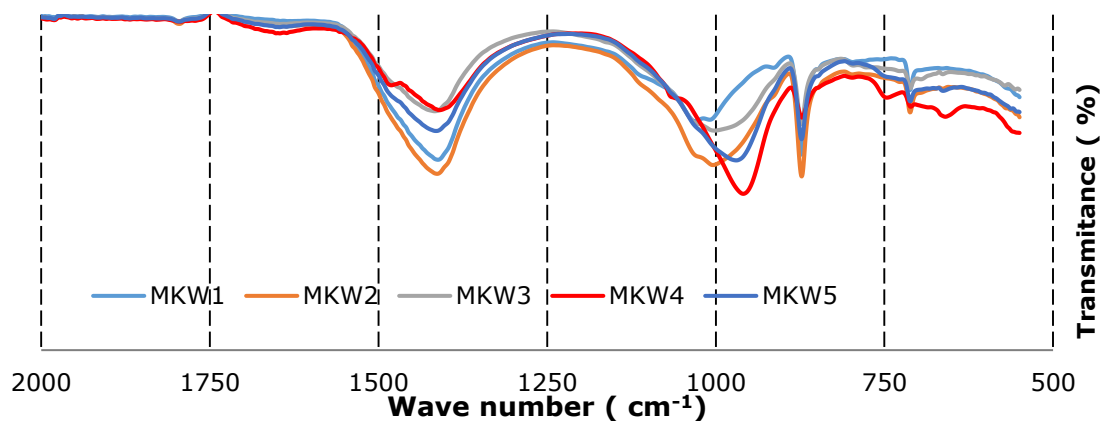


Figure 4.14: FTIR spectra for MKW geopolymer system

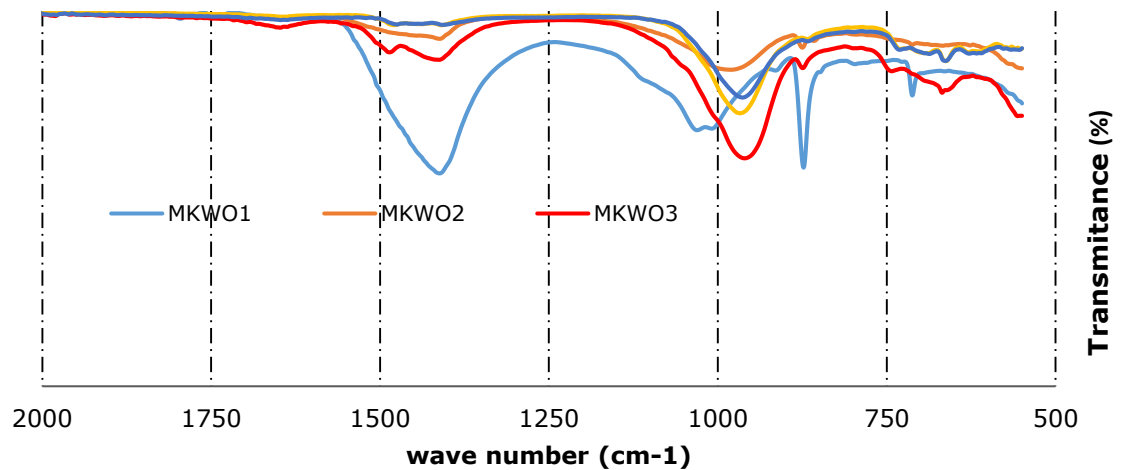


Figure 4.15: FTIR spectra for MKO geopolymer system

Figure 4.16 shows the XRD patterns for metakaolin- which indicate the presence of quartz and some other phases. The unanticipated finding in the X-ray diffraction patterns for this system was the absence of any peaks or patterns related to geopolymer gels such as sodalite or katoite which may correlate with the XRD analysis of metakaolin and the absence of any kaolinite phases.

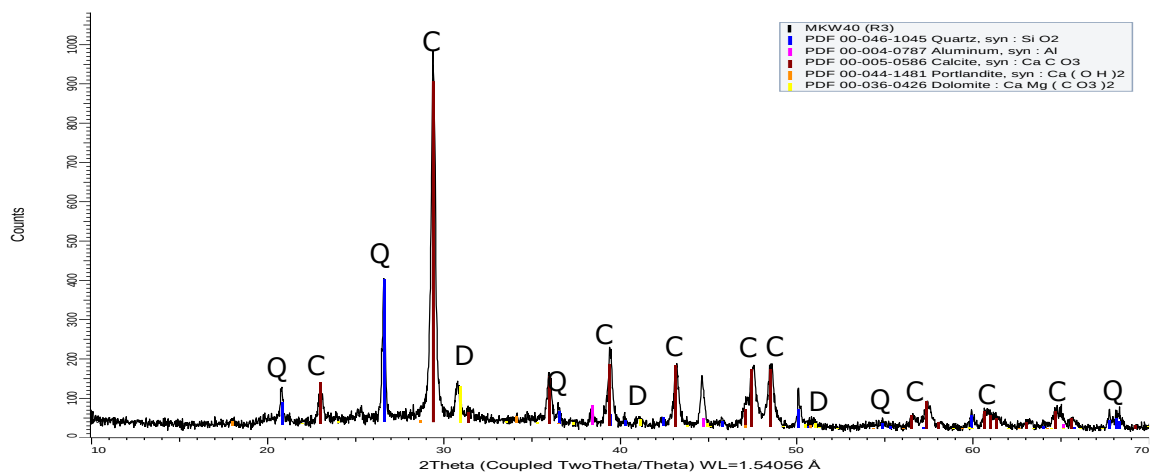


Figure 4.16: X-ray diffraction patterns of MKW geopolymers

4.6.5 The effect of changes in geopolymer formulation on macroscopic properties changes and the leachability behaviour in K-waste geopolymer systems

4.6.5.1 Macroscopic changes and leachability behaviour of K-waste system

The impact of changing formulation of K-Waste geopolymers on the macroscopic properties of produced solid matrixes has been investigated in order to understand the effect of alkali activator concentration and water: solid ratio on the internal structure properties and its reflection on the leachability behavior of K-waste geopolymers.

The relation between changing the formulation and macroscopic properties such as water absorption, total void volume is presented in Figure 4.17 for KW system and Figure 4.18 for the KO system. The results indicate that there is a direct impact of changing the formulation on changing the microstructure properties of formulated geopolymers (porosity and density properties) which was expected to affect its performance in immobilization the HMs and encapsulation of TPH.

The obtained results were found useful in choosing the optimum geopolymer recipes that exhibited a higher degree of geopolymerisation and expected to reduce the efflorescence issue. Figure 4.17 presents the experimental data obtained using the KW geopolymer system.

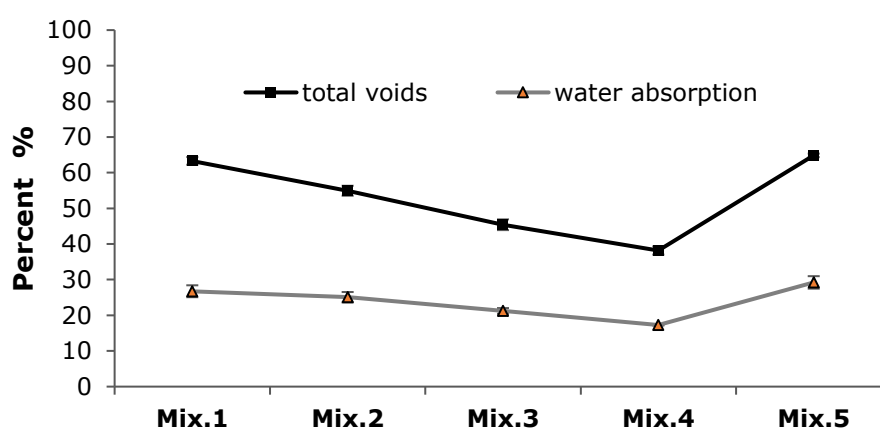


Figure 4.17: Effect of geopolymer formulation on water Absorption and total voids volume properties in KW geopolymer recipes. The error bar represents the standard deviation from the mean for 5 data points in triplicate

The changing of formulation has a significant relationship with internal structure changes. The changing in formulation was found effected the water absorption as the p-value <0.002 and effected the total void volumes in the level p-value < 0.001.

The obtained results were found useful in choosing of the optimum geopolymer recipes in this system. Optimum recipe selected in the bases of the recipe that exhibited a higher degree of geopolymerisation, lower water absorption and lower total voids within its framework.

The data in Figure 4.17 showed that Mixes 3 and 4 have the lowest water absorption and total voids volume and expected to have the lowest porosity and pore size as reported by Farhana et al., (2014) and Liew et al., (2016). Mix.3 and mix.4 would also be expected to have the densest homogeneous structure, lowest internal porosity among proposed recipes in this system, and therefore would be expected to have lower leachability and efflorescence problems and better durability properties in these recipes.

The data in Figure 4.18 shows that the changes in formulation of KO geopolymer systems affected the water absorption value and total void volume values in p-value level (<0.001), and that recipe KO2 and KO3 have the lower values of water absorption and voids volume, thus indicating that they have a similar porosity property.

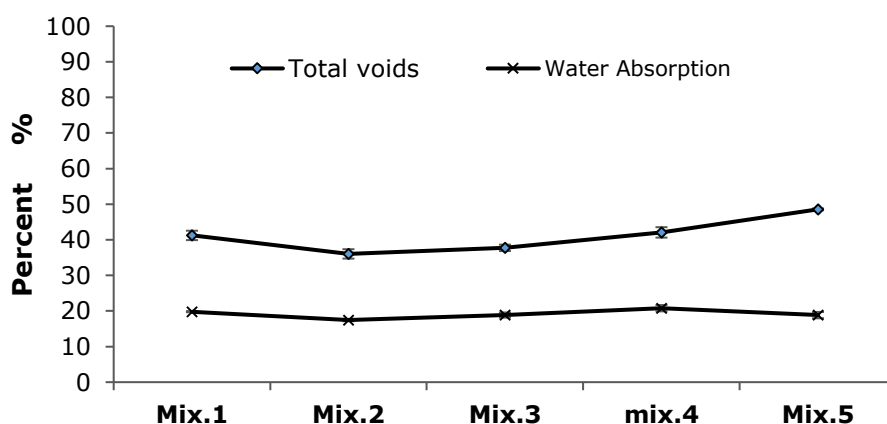


Figure 4.18: Effect of geopolymer formulation on water Absorption and total voids volume properties in KO geopolymer recipes. The error bar represents the standard deviation from the mean for 5 data points in triplicate.

The results show that, despite the higher petroleum hydrocarbon content in the KO geopolymer samples comparing with KW geopolymers, it is having lower water absorption and voids volume, which may attribute to the influence of water: solid ratio used in this system (0.2 in KO comparing with 0.3 in KW systems). Similar conclusion reported by Cui and Wang, (2019) linking the effect of using lower water: solid value with the lower porosity values and better mechanical properties. The results harmonize completely with the conclusions obtained by many authors (Liew et al., (2011); Azizli et al., (2014)).

4.3.5.2 Macroscopic changes and leachability behaviour of MK-waste system

The most obvious finding emerges from the study of the impact of changing geopolymer formulation in MKW system was the higher voids volume and water absorption percentage within the MKW geopolymer systems networks in the level (p -value <0.016 , and <0.054 respectively) as illustrated in Figure 4.19. It was observed that the water absorption and total voids in MKW systems increased between 25-100 % when compared with recipes prepared by KW geopolymers. These results expected to reflect negatively on the microstructure and porosity properties for MKW systems and expected to produce geopolymers with lower strength and durability properties.

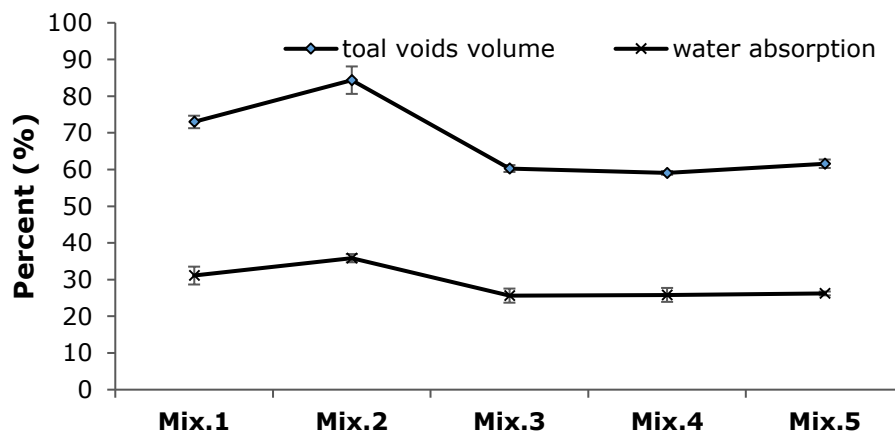


Figure 4.19: Water absorption and total voids volume in MKW geopolymer recipes. The error bar represents the standard deviation from the mean for 5 data points in triplicate.

The results accord with the finding of earlier observations, which attributed this to the drying shrinkage occurs during curing of metakaolin geopolymers at ambient temperature. As reported by Kuenzel et al., (2012), the dry shrinkage led to losing the structural integrity and increasing the porosity within metakaolin geopolymers. Similar studies also linked the dry shrinkage occurred in these systems with formation of early-age cracking which highly detrimental to the durability of these systems as reported by Palumbo et al., (2017).

The obtained results in MKO geopolymer system can be observed in Figure 4.20. In general, there are significant dependence of water absorption and voids volume percentage on the changing of formulation of MKO on the level of ($p < 0.001$) in both macro properties.

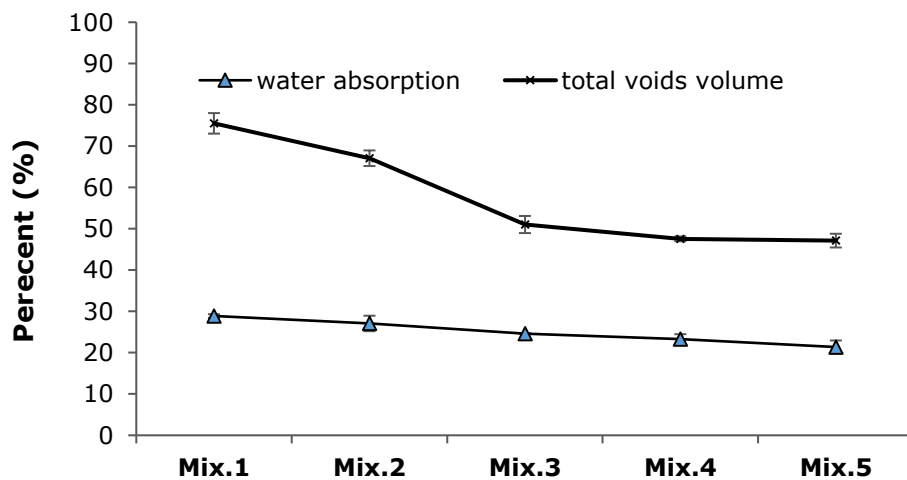


Figure 4.20: Water Absorption and total voids volume in MKO geopolymer recipes. The error bar represents the standard deviation from the mean for 5 data pints in triplicate.

The results indicate that recipe (MKO3, MKO4 and MKO5) have the lower ability to absorb water molecules and have the lowest voids volume and expected to have the similar internal structure characteristics. The obtained results in this system confirm the effect of use lower water: solid ratio in formation of solid system with lower water absorption and voids volume.

4.3.6 Effect of geopolymer formulation on leachability behaviour and the tendency to efflorescence in K- waste systems

The leachability test was used as a quantitative measure to estimate the success of S/S of drilling waste using kaolin and metakaolin binders. The obtained data used also to detect the metals and compounds remain un-combined within the geopolymer networks which may leachate and cause the efflorescence problems. The data also used to select the optimum geopolymer formula which has lower ion mobility and expected to have a lower tendency toward efflorescence issues within the produced solidified waste systems.

The results in Figure 4.21 shows no significant difference in the amount of dissolved salts in geopolymer formulas (Mix.1 Mix.2) in KW and (Mix. 1, Mix.2 and Mix.3) and KO systems, and gradual increase in the amount of dissolved salts in recipes (Mix. 3, Mix.4 and Mix.5) which sequentially will have higher tendency to cause the efflorescence issue.

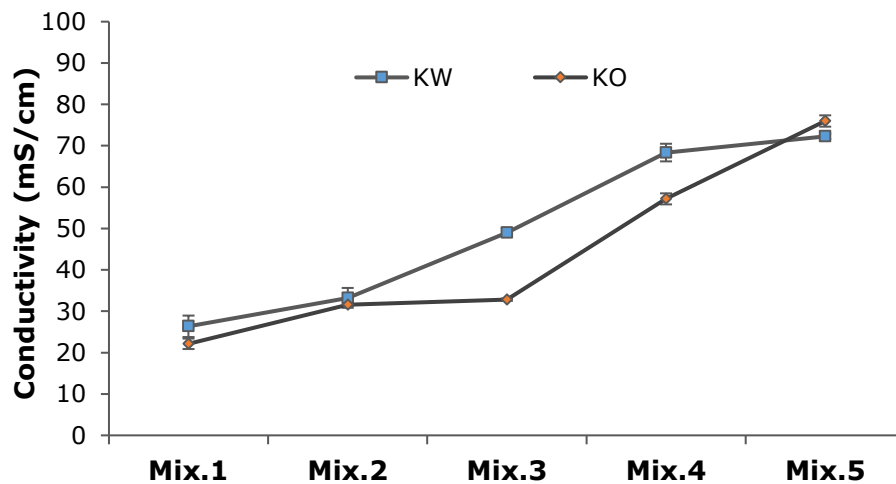


Figure 4.21: Tendency toward efflorescence KW and KO systems. The error bar represents the standard deviation from the mean for 5 data points in triplicate.

The results illustrate that Mix. 4 and Mix.5 in (KW and KO systems) have high ability to leach dissolved salts, which might be attributed to open geopolymer microstructure network in these mixtures and the higher amount of unreacted raw materials and alkali activator in these systems when compared with the other mixtures (Mix.1, Mix.2 and

Mix.3) in both systems. The open internal microstructure reflects negatively on the porosity, leachability behaviour and mechanical integrity of the obtained solidified waste KW and KO geopolymer systems.

In the same results, as illustrated in Figure 4.22 for KW, and Figure 4.23 for KO system it is noticed that the most leachable species in solutions derived from KW and KO geopolymers is Na^+ . The leaching of Na^+ was found to increase with increase of alkali activator concentration in recipes in KW system and Mix.3, Mix.4 and Mix. 5 in KO systems which will represent a potential danger as regards the efflorescence occurrence as concluded in previous research (Zhang et al., 2014) who found that the excess alkali activator concentration results in efflorescence problems which in the long term effects the integrity and strength development of geopolymer matrices.

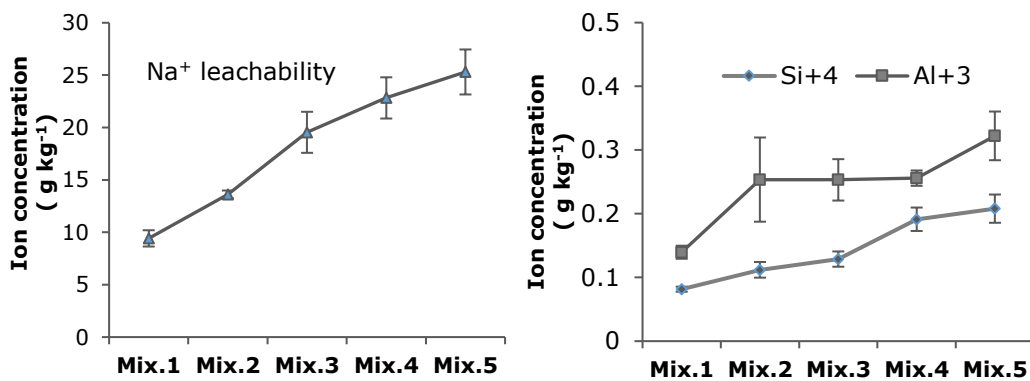


Figure 4.22. (a). leachability of Na^+ ion **(b)** Silicon and aluminium ions from KW geopolymer systems

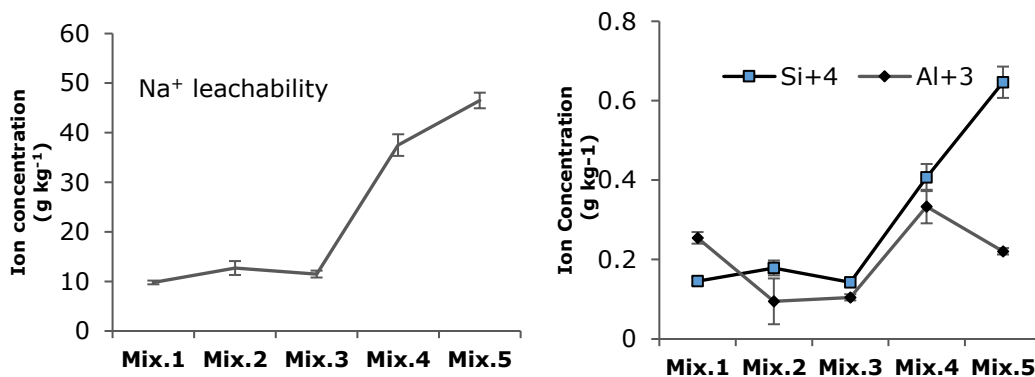


Figure 4.23 (a). leachability of Na^+ ion **(b)** Silicon and aluminium ions from KO geopolymer systems. The error bar represents the standard deviation from the mean for 5 data points in triplicate.

Also, it was interesting to note that the use of high concentration of alkali activator in Mix.4 and Mix.5 in both systems were found to cause presence of quantities of

aluminium and silicate ions in its dissolved form (Figure 4.22b) in KW and (Figure 4.22b) in KO geopolymer systems. A possible explanation for this might be that these ions produced by the action of strong NaOH solution in these mixtures during the dissolution of raw materials in early stages of the geopolymer reactions and remain unreacted or combined within the geopolymer network.

4.3.7 Effect of geopolymer formulation on Leachability behaviour and the tendency to efflorescence in MK- waste systems

The results obtained from the analysis leachate salts in MKW and MKO systems was identical with those obtained with KW and KO systems. In both MK-waste systems it is found that the increasing in alkali activator effect significantly on the ability of geopolymers to leachate dissolved salts and cause efflorescence problem in the level of p -value < 0.001 . Figure 4.24 show that the tendency towered efflorescence issue MK-waste systems are increased with the increasing of alkali activator concentration in the system and that the increase of alkali activator solution have negative effect on the leachability behaviour of proposed MK-waste geopolymers.

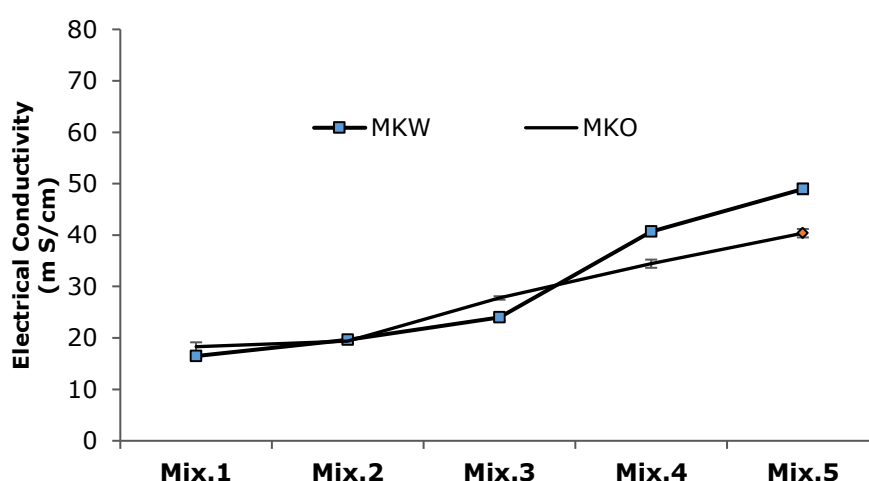


Figure 4.24: Tendency towered efflorescence MKW and MKO systems. The error bar represents the standard deviation from the mean for 5 data pints in triplicate.

The results show that the dissolved ion contents of MKW leachate were higher than those of MKO geopolymer in recipes Mix.3, Mix 4 and Mix. 5. In Figure 4.25a and Figure 4.26a it is a clear that the most leachable species in solutions derived from MKW and

solutions of MKO was the sodium ion which derived mainly for the alkali activator solution with may use as evidence for the destructive effect of using high alkali activator concentrations. It is also noticed in Figure 4.25b and 4.26b that the leachate of both systems has high amounts of aluminium in form of solvated ion which increased in Mix.4 and Mix.5 by the increase of NaOH concentration indicating uncomplete geopolymer reaction in these systems.

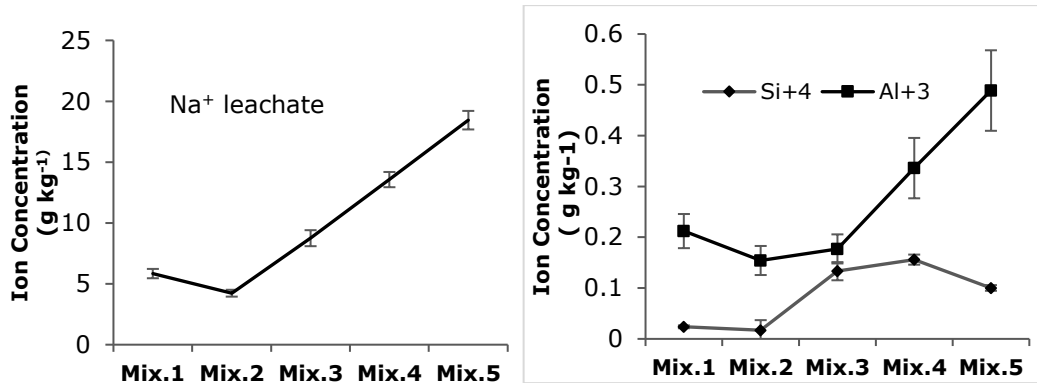


Figure 4.25. (a). leachability of Na⁺ ion **(b)** leachability of Al³⁺ and Si⁴⁺ ions from MKW geopolymer systems

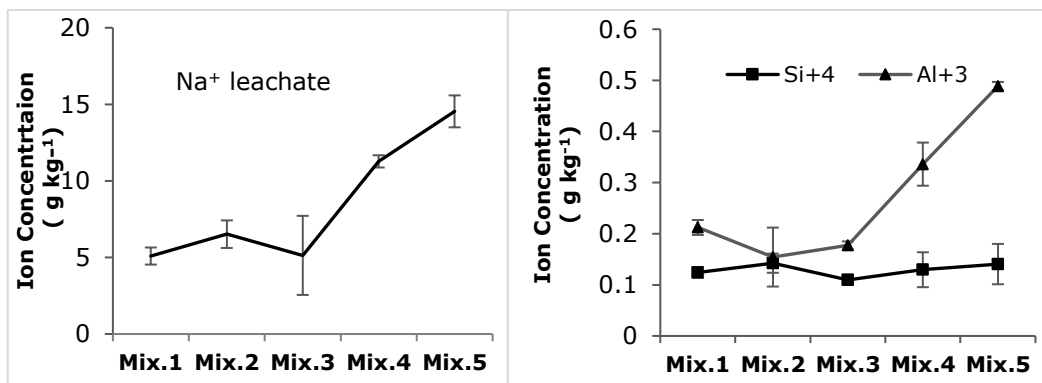


Figure 4.26 (a). leachability of Na⁺ ion **(b)** leachability of Al³⁺ and Si⁴⁺ ions from MKO geopolymer systems. The error bar represents the standard deviation from the mean for 5 data pints in triplicate.

4.3.8 Efficiency of geopolymer systems in immobilization of heavy metals in K-waste systems

The important result observed from the heavy metals leaching tests that all proposed geopolymer recipes were efficient in immobilizing of toxic and heavy metal ions existence within the drilling waste samples, both systems have high efficiency in stabilisation of those ions within its geopolymer network. Table 4.5 compare the concentration of heavy and toxic metals in solid geopolymer mortars and the average

value in its leachate after 28 days of solidification of proposed KW3 and KO3. In the leachate of all KW and KO geopolymer mortars (Mix.1 to Mix.5) the concentration of heavy and toxic ions in water leachate were found in very low concentrations and lower than limit values for compliance leaching test using BS EN 12457 and criteria for granular waste acceptable at landfills (Annex 2003/22/EC). Both of treated systems could be considered as inert waste.

Table 4.5: Summary of TCLP leaching values for solidified KW and KO geopolymer Systems

Ion (mg. kg⁻¹)	Cr	Fe	Ni	Cu	Zn	As	Cd	Ba	Pb
Raw material	21	3756	10	13	28	2.3	0.16	423	42.8
KW3 Leachate	0.38	0.38	0.0	0.14	0.03	0.16	0.00	0.07	0.01
Raw Material	18	4188	9	13	31	3	0.0	3854	25
KO3 Leachate	0.3	0.3	0	0.1	0.0	0.1	0.0	0.07	0.01
Inert waste	0.50	NL	0.4	2.0	4.0	0.5	0.04	20	0.50
Stable nonreactive hazardous waste	10	NL	10	50	50	2	1	100	10
Hazardous waste landfill	70	NL	40	100	200	25	5	300	50

NL = not listed

4.3.9 Efficiency of Geopolymer systems in immobilization of heavy metals in MK-waste systems

Table 4.6 compare the leaching results of the geopolymer samples prepared using MKW and MKO systems with the original content of each recipe in the solid form. The results showed that most of heavy and toxic metals were fully retained in the geopolymers matrix. It is clear that all proposed recipes efficient enough to stabilise the heavy metals.

Table 4.6: Summary of TCLP leaching values for solidified MKW and MKO geopolymer Systems

Ion (mg. kg⁻¹)	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Ba	Pb
KW geopolymer systems											
Raw material	40	35.8	63	4277	15	16	33	2.4	0.20	622	45
MKW3 Leachate	0.0	1.9	0.0	0.34	0.0	0.16	0.04	0.19	0.0	0.04	0.0
KO geopolymer systems											
Raw Material	23	18	68	4188	9	13	31	3	0.0	3854	25
MKO3 Leachate	1.0	1.0	0.0	0.33	0.0	0.1	0.02	0.1	0.0	0.1	0.0
<i>Criteria for granular waste acceptable at landfills</i>											
Inert waste	NL	0.50	NL	NL	0.4	2.0	4.0	0.5	0.04	20	0.50
Stable nonreactive hazardous waste	NL	10	NL	NL	10	50	50	2	1	100	10
Hazardous waste landfill	NL	70	NL	NL	40	100	200	25	5	300	50

NL = not listed

The leachate test results confirm that all KW, KO, MKW and MKO geopolymer systems was efficient in immobilisation of toxic metals under the allowable limits. According to the HMs leachate, Kaolin-waste systems (KW and KO) was found more efficient in immobilisation of HMs and transform the drilling waste to inert waste landfill. Metakaolin-waste systems (MKW3 and MKO3) was classified as stable non-reactive hazardous waste using the same criteria due to the leachability of higher chromium ion concentration from those systems.

This finding broadly supports the work of other studies in similar area linking the performance of solidified matrix in immobilisation of heavy metals with the superior properties of geopolymers such as the abundance of the very small pores, low permeability, very high pH value, good chemical stability, and a three-dimensional microstructure. In this study, the high efficiency K-waste may attribute to the formation on kaolin/zeolite geopolymer composed from phases such as sodalite, and formation of calcium-based geopolymer such as katoite and other phases such as Hydrotalcites within the S/S systems. All mentioned phases characterized by unique characteristics such as cation / anion exchange ability, high surface area and adsorption capacity, surface basicity as reported by many researches (Parker e al., 1995; Perotti et al., 2014), these properties assist the immobilisation of HMs in solidified matrices through different mechanisms such as chemical bonding, precipitation or physical encapsulation within the binder-waste geopolymer S/S systems as reported by Vu and Gowripalan, (2018).

The most obvious finding emerges from the study of the impact of changing formulation on the internal network structure of produced geopolymers, and from the comparison between the data obtained from K-waste and MK-waste geopolymer systems are: -

- Although metakaolin is more reactive than kaolin in the geopolymerization process, the interesting finding emerged from this study is that Kaolin-waste

geopolymers produced more homogeneous system in KW and KO systems, have lower water absorption and total voids volume comparing with MKW and MKO which indicate that these systems have fewer capillary pores content and expected to present denser geopolymers with lower porosity and permeability. The obtained microstructure properties in K-waste systems expected to reflect positively in the leachability and durability properties of solidified systems. The results further support the results obtained by Phair et al. (2004) who concluded that kaolin is more efficient in immobilisation of HMs than metakaolin due the higher surface area and better microstructure properties.

- The water: solid ratio has direct effect on the porosity level of the hardened geopolymer paste, and using of lower water: solid ratio will increase the concentration of alkali activator and its viscosity and improve the workability of the geopolymer paste. The lower water: solid ratio found to produce homogeneous matrices with lower porosity and compact structure thus leads to high durability properties. This finding supports evidence from previous observations reported by Liew et al., (2011) who concluded the significant effect of lower water: solid ratio on improvement of microstructure properties and the compressive strength of hardened geopolymer paste
- The statistics analysis using Duncan's new multiple range test found that no significant differences between geopolymers recipes (Mix.3 & Mix.4) in all geopolymer systems, this allowing select recipe (Mix.3) as optimum geopolymer formulation and expected to have denser structure, lower cracks and voids and expected to be more sustainable and economic.

4.3.10 Efficiency of geopolymer systems in encapsulation of organic materials

TPH concentrations were measured in the leachates extracted from the untreated raw materials WBM and OBM, and from the treated samples KW3 and KO3 after 28 day

curing period are presented in Table 4.8. The chromatograms obtained by GC-FID analysis of both untreated and treated drilling waste are also presented in appendix.3. Both KW3 and KO3 system present significantly high percentage reduction of fraction 2 petroleum hydrocarbons (C10-C16), and wide range of reduction percentage values for heavier petroleum hydrocarbons fraction 3 (C16-C34) ranging from 31 to 100%. The leachate from KW3 contains very low concentration of heavy aliphatic compounds (C20-C24, C26, C28, C29 and C31). Also, the leachate from KO3 contains very low concentrations of the same fraction (C20, C23, C26, C28, C29, C31 and C32).

The overall reduction of TPH concentrations upon treatment through addition of additives and geopolymerisation using kaolin ranged between 91% in KW3 system and 96 % in KO3 system as shown in table.4.7.

Table 4.7: Leachability of petroleum hydrocarbons from KW & KO solidified systems and the overall reduction performance

Material	TPH leachability (mg kg⁻¹)
WBM raw material	5616
OBM raw material	12969
KW3 system	518
KO3 System	241
<i>Criteria for granular waste acceptable at landfills</i>	
Inert Waste Landfill	500
Stable nonreactive hazardous waste & nonhazardous waste co-disposed with (SNRHW)	800
Hazardous waste landfill	1000
<i>TPH leachability reduction (%)</i>	
KW3 system	91
KO3 System	96

The result clearly indicates the feasibility of treatment of both types of drilling waste (WBM waste contains 1.47 wt. % TOC approx. 14700 mg kg⁻¹), and (OBM waste contains 8.56 wt. % TOC approx. 85600 mg kg⁻¹) using S/S techniques through geopolymerisation by kaolin and lime as additives. Both solidified systems, KW and KO managed to encapsulate petroleum hydrocarbons and transform the drilling waste to inert waste landfill or stable non-reactive hazardous waste according to the UK landfill acceptance criteria. The corresponding limit values for compliance leaching tests using

BS EN 12457, are 500, 800 and 1000 mg kg⁻¹ for inert waste, stable non-reactive hazardous waste (to be disposed in non-hazardous landfill) and hazardous waste, respectively as shown in Table 4.7.

Table 4.8: Concentrations of petroleum hydrocarbon leachate of raw drilling waste treated KW3 and KO3 geopolymer system and efficiency of geopolymer S/S systems.

TPH Fraction	TPH mg/Kg				% Reduction of TPH in leachate	
	WBM	OBM	KW3	KO3	KW	KO
n-C10	13.5	0	0	0	100	
n-C11	5.40	0	0	0	100	
n-C12	10.1	22	7	0	27	100
n-C13	5.23	110	0	0	100	100
n-C14	7.31	471	0	0	100	100
n-C15	456	1142	0	0	100	100
n-C16	672	1653	0	0	100	100
n-C17	770	1835	0	0	100	100
n-C18	690	1609	0	0	100	100
n-C19	673	1471	0	0	100	100
n-C20	503	1169	18	12	96	99
n-C21	416	944	19	0	95	100
n-C22	348	772	13	0	96	100
n-C23	590	603	409	158	31	74
n-C24	195	487	0	0	100	100
n-C25	27	43	0	0	100	100
n-C26	12.6	24	11	13	13	47
n-C27	1.59	196	0	0	100	100
n-C28	100	132	15	19	85	86
n-C29	43	52	16	19	64	63
n-C30	27.9	58	0	0	100	100
n-C31	40.0	91	10	13	75	86
n-C32	0.97	31	0	7	100	78
n-C33	1.60	7	0	0	100	100
n-C34	1.54	15	0	0	100	100
n-C35	2.15	12	0	0	100	100
n-C36	3.47	20	0	0	100	100

The results indicate that the solidified waste geopolymers encapsulate light and heavy petroleum hydrocarbon, and managed to stabilise the organic contaminates within geopolymer networks depict the high concentration of organic compounds (C10-C36) in the leachate of waste raw materials.

The efficiency of produced geopolymers in encapsulation of petroleum hydrocarbon using KW and KO systems may correlated with the formation of sodalite and Katoite phases in this geopolymer systems as shown in XRD analysis results, and to the unique internal surface areas possessed in these phases which assist the adsorption capacity of organic materials as concluded by Asgari et al., (2018). Furthermore, the reduction in concentrations of petroleum hydrocarbon compounds may attributed to the effect of addition of hydrated lime to Kaolin based geopolymer. As concluded by Schifano and Thurston., (2007), Addition of lime resulted in significant decreases in total concentrations and leachability of petroleum hydrocarbon compounds through volatilization mechanism or encapsulation mechanism where the petroleum hydrocarbons trapped within the solid matrix. Similar results obtained by Al-Ansary and Al-Tabbaa, (2007) support the effect of lime addition in reducing of leachability of petroleum hydrocarbons from PC based S/S system.

4.4 Conclusions

The primary objectives of this study were to solidify and stabilise the contaminated drilling waste using geopolymer technologies. The experimental work was carried out using different geopolymer recipes composed from binders like Kaolin, calcined kaolin (metakaolin), and two types from drilling waste contains different contamination levels and additives like alkali activator (NaOH) and hydrated lime as additive material. Through the results obtained from different physical, chemical and microstructure analysis, the following conclusions can be drawn:

- Geopolymers composed from Kaolin –drilling waste have been successfully produced using local natural materials and can be used as a matrix for fixation of heavy metals and encapsulation of hydrocarbons offering a sustainable and cost-effective approach that brings environmental and economic benefits.
- The highest degree of geopolymerisation, the optimum microstructure properties and leachability behaviour was achieved using the formula KW3 for treatment of drilling waste contains (0.59 wt. % TOC), and the formula KO3 for treatment of drilling waste contain higher TPH concentrations (3.42 wt. % TOC).
- The curing regime used to produce Kaolin-waste geopolymers was simulation of real condition on Libyan Desert during the summer period, which prove the feasibility of using geopolymer technology in practical applications for management of drilling waste generated during the oil and gas industry activities in Libya.
- The FTIR and XRD spectroscopy corroborate the transformation of kaolin-waste mixtures to geopolymers and the formation of new phases such as hydrosodalite. The results confirme formation of kaolin/zeolite based geopolymers (El-Eswed et al., 2015; Marsha et al., 2018). which characterized by denser lattice, higher stability and high specific surface area allowing for higher sorption and adsorption capacity. The results

also confirm formation of katoite and Hydrotalcites phases which have unique cation-exchange ability, anion-exchange ability, surface adsorption capacity and surface basicity reflected in high performance in immobilization of HMs and encapsulation of petroleum hydrocarbons.

- The leachability results indicated that KW3 and KO3 recipes effectively immobilized the HMs and encapsulated the petroleum hydrocarbons within kaolin/zeolite based geopolymers and convert the hazardous waste to stable nonreactive hazardous waste (SNRHW) acceptable for safe landfill or reuse in various environmental management options for
- K-waste geopolymers exhibited a higher degree of geopolymerisation and have the lower water absorption and total voids volume comparing with MK-waste geopolymers when cured at ambient Libyan Desert climate condition, indicating that these systems have better internal structure properties, fewer capillary pores content, lower porosity and permeability which reflected positively in the leachability behaviour and expected to be more durable.
- Alkali activator NaOH has the significant effect on the transformation of raw materials to geopolymers, increase along with the increase within the range (8-10 M) for Kaolin and metakaolin –WBM systems and (8-9 M) for Kaolin and metakaolin-OBM systems. Also, the higher alkali content was noticeable affected negatively on the performance of produced geopolymers and expose it to efflorescence and cause internal structural weakness.
- Addition of hydrated lime enhance the transformation of raw materials (kaolin and drilling waste) to solid matrix and strengthen the produced geopolymers by forming amorously structured CASH gel. Furthermore, addition of lime significantly increased

pH value, decreased cation exchange capacity, heavy metals mobility and the leachability of hydrocarbon from geopolymer-waste systems.

- Water: solid ratio plays very important rule in the viscosity, flow and the cohesiveness of geopolymers and the use of lower ratio reflects positive in the internal microstructure properties of geopolymers by decreasing the voids and cracks inside
- Drilling waste composition and contamination level by petroleum hydrocarbons plays an important role in the microstructure properties, leachability behaviour and the strength of the final solidified matrix which affects the selection of the appropriate waste management application (reuse or safe landfill) for these types of waste.

These results obtained in this chapter add to the rapidly expanding field of using geopolymers in various environmental management options, and presented a useful assessment of the effectiveness of using natural kaolin clay as a binder in the S/S of drilling waste contains low-medium levels of HMs and high TPH values. It highlighted the effect of alkali activator and lime in producing S/S systems through geopolymerisation and the important effect of lowering water: solid ratio to produce geopolymers with better microstructure properties for use in environmental applications.

The findings of this research also support the observations and conclusions of previous studies related to the effect of metal oxide ratio ($\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$), ($\text{SiO}_2 : \text{Al}_2\text{O}_3$), ($\text{H}_2\text{O} : \text{Na}_2\text{O}$) and the effect of addition of Na_2SiO_3 and particle size on the physical and mechanical properties of geopolymers and the effect of curing time to judge the actual physical, mechanical and leachability properties of geopolymers. These research results can be used as ground information for further studies to improve the performance of Kaolin-waste geopolymers and its durability.

Chapter 5: Effect of additives, binder particle size and aging on the microstructure and mechanical properties of geopolymers

5.1 Introduction

The focus of this chapter is to test factors that enhance the geopolymerisation reaction to improve the physical, chemical and durability properties for the successful recipes developed in Chapter 4. This chapter also will examine the durability of the geopolymer-waste systems in the Libyan Desert climate to predict the effect of weather on the strength and leachability of the solidified matrices and to compare their stability with similar matrices prepared using Portland cement.

Different additives can be used to improve the geopolymerisation reaction and the transformation of aluminosilicate materials to gel. Yip et al., (2008) studied the effect of adding calcium to a metakaolin geopolymer system and found that addition of 20% calcium improves the strength and formed calcium silicon hydrate (CSH) gel in conjunction with the sodium silicon aluminium hydrate gel (NSAH), improving the mechanical properties of the geopolymers.

Christine et al., (2003) found that addition of soluble silicate significantly increases the dissolution of metakaolin releasing silicate needed to form the aluminosilicate gel. Fansuri et al., (2010), and Wang et al., (2012) both reported that the presence of sodium silicate Na_2SiO_3 led to the formation of amorphous structure within geopolymers and enhanced its strength development, they also concluded that further increasing sodium silicate resulted in a loss of compressive strength during the early stages of geopolymerisation.

A study by Gao., (2013) reported that the addition of sodium silicate decreased geopolymer setting time, promoting the reaction and producing geopolymers with smaller cumulative pore volume and higher mesoporous volume both of which reflected

positively on adsorption properties of geopolymers produced for environmental applications.

To date, few reports are available on the influence of particle size on the properties of kaolin-based geopolymers. The effect of the fineness of the raw material on the geopolymerisation reaction rate and microstructure properties has however been investigated using binders such as fly ash or red mud and other aluminosilicate materials. Szabo et al., (2017) reported that the use of fly ash with smaller particle size, and therefore increased specific surface area, enhanced the reactivity resulting in increased formation of aluminosilicate gel. Assi et al., (2018) reported that microstructural changes in fly ash geopolymers are a function of the fly ash source and its particle size distribution with finer particles having a positive impact on microstructural properties and long-term geopolymer performance. A study by Antoni et al., (2015) concluded that the use of finer particle size of calcined mud also enhanced the reactivity of the raw materials, resulting in higher compressive strength of geopolymers.

There is a need to explore the possibilities provided by using kaolin clay binder in the treatment of drilling waste using S/S techniques to enable recommendations to be made for future research using the most appropriate recipes. Therefore, two geopolymer-waste formulations were chosen in order to investigate whether improvements could be made to their microstructural properties and strength. Their properties were compared to the same mixes made using ordinary Portland cement OPC.

The specific objectives were to:

- (i) Test whether the physical and mechanical properties of the geopolymers can be improved by the addition of sodium silicate and/or changing the particle size of the kaolin binder and,

- (ii) Investigate the effect of climate on the physical and mechanical properties and the leachability of the optimum geopolymers after aging for 1 year in the Libyan Desert.

5.2 Experimental Approach

5.2.1 Materials and methods

Two kaolin-waste formulations, KW3 and KO3, were chosen in order to investigate the effect of the addition of sodium silicate, and the role of binder particle size in the improvement of microstructure properties and strength. The effect of aging on the durability and leaching behaviour of the solidified systems was also tested. Both recipes were formulated using natural kaolin binder with chemical composition and phase mineralogy as described in Section 4.2.1.2 of Chapter 4 using drilling waste samples WBM and OBM that have the physical properties, chemical composition and phase mineralogy described in Section 3.3.1 of Chapter 3. Both recipes have similar quantity of additives (lime and aggregate) and have a technical specification as described in Section 2.1.3, Chapter 2 and were activated by NaOH. Ordinary Portland cement (see Section 4.2.1.2, Chapter 4) that is commonly used in Libya for construction purpose was used as a binder to prepare PC-waste systems for comparison purposes.

The method described in Section 4.2.3, Chapter 4 was used to mix the geopolymers and the PC equivalent samples with the modification of using water to replace the alkaline activator in PC-waste systems. To examine the effect of adding active silicate to the geopolymer recipes, high purity sodium silicate Na_2SiO_3 (Fisher Scientific UK) was used. The alkali activator in these experiments was therefore a mixture of NaOH and Na_2SiO_3 . The addition of sodium silicate to KW and KO systems led to a change in the chemical composition and chemical formula of the geopolymer recipes. The modified recipes designated as KWNS and KONS, are shown in Table 5.1.

Table 5.1: Chemical formula and mole ratio of the modified geopolymer recipes.

	Mole ratio					
	SiO ₂ :Al ₂ O ₃	Na ₂ O:Al ₂ O ₃	Na ₂ O:SiO ₂	Na ₂ O:CaO	CaO:SiO ₂	H ₂ O:Na ₂ O
KWNS	3.6	1.0	0.3	0.3	1.0	13.0
	<i>Chemical formula: 1.0Na₂O. 3.6SiO₂. 1.0Al₂O₃. 3.6CaO. 13.2H₂O</i>					
KONS	3.8	1.0	0.24	0.3	1.0	10.0
	<i>Chemical formula: 1.0Na₂O. 4.2SiO₂. 1.1Al₂O₃. 3.9CaO. 10.0H₂O</i>					

To investigate the effect of using finer binder particle size on the microstructural and mechanical properties of the geopolymers, two-particle size fractions were prepared by sieving kaolin clay through 1000 μm and 400 μm sieves. The fraction passed through the 1000 μm sieve was used to prepare KW and KO recipe designated in this study as KW1000 and KO1000, and which passed through 400 μm sieves was assigned in the experiments as KW400 and KO400. Drilling waste and all other additives were used as received and prepared as described in Section 2.1.1 in Chapter 2.

After mixing and shaking the samples as described in Section 4.2.3, Chapter 4, all samples were cast in moulds as described in Section 4.2.4, Chapter 4 before curing under conditions simulating the Libyan Desert climate during the summer period described in Section 4.2.5, Chapter 4. Samples were tested after 28 days curing.

5.2.2 Testing

The physical effect of adding Na₂SiO₃, and using different particle size of kaolin binder on water adsorption, bulk density and percentage pore volume were examined as described in Sections 2.2.2, 2.2.3 and 2.2.4 of Chapter 2. Acid attack (see Section 2.2.1, Chapter 2) was used to monitor the effect of adding Na₂SiO₃ and the effect of using finer particle size in enhancement of formation of geopolymer gel. In this test, approximately 1 gram of geopolymer paste (in triplicate) was taken and immersed in 250 ml of hydrochloric acid: water solution (1:20 v/v) to dissolve the gels generated during the geopolymerisation reaction. After 1, 3, 7, 14, 25 and 28 days, the mixture was stirred with a plastic magnetic stirrer for three hours, after which it was filtered and washed many times with MQ water. The insoluble residue was burned in a muffle

furnace for 2 hours, cooled to room temperature, and the quantity of remaining materials weighed and recorded to determine the amount of non-activated oxides. To measure the gel content and deduce the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio in the geopolymer gel during the reaction, the acid solution contains the metals incorporated in gel formation were filtered through a $0.45\ \mu\text{m}$ filter before analysis by ICP-MS. The metal content was calculated and presented as Si:Al or $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio and used to monitor the reaction kinetics.

Leachability of the geopolymers was evaluated using ICP-MS for determination of heavy and toxic metals and GC-FID for measuring of petroleum hydrocarbons as described in Sections 2.2.7, 2.2.8 and 2.2.9 of Chapter 2. The changes in internal structure was investigated using the UVP test described in Section 2.2.5, Chapter 2 to examine the homogeneity, and predict the strength of both geopolymer and cement-waste system after 28 days. It was also used to evaluate the effect of aging of S/S systems cured in real weather changes in the Libyan Desert. Unconfined compression test UCT (see Section 2.2.6, Chapter 2) was used to evaluate the effect of adding Na_2SiO_3 or using finer kaolin particle size. It is also used as an indication of the effect of aging in all geopolymers and PC-waste systems.

5.3 Results and Discussions

5.3.1 Effect of addition of Na_2SiO_3 on enhancement of geopolymer gel formation

The degree of geopolymerisation reaction after curing of all systems for 28 days was used to monitor the development of geopolymer gel.

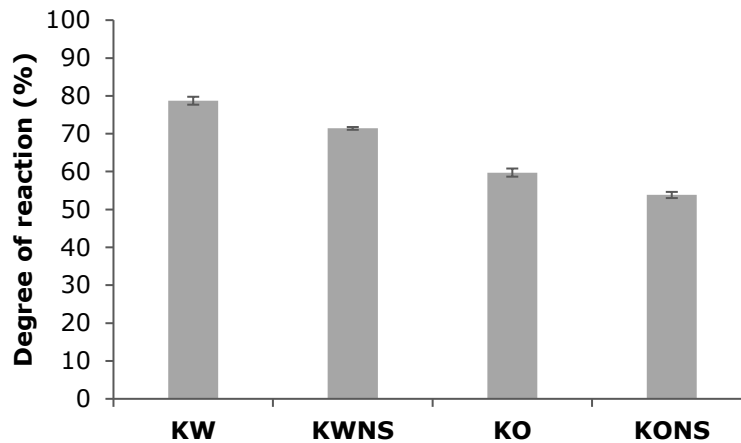


Figure 5.1: Effect of adding Na_2SiO_3 to KW and KO geopolymer systems. The Figure shows the destructive effect resulting from adding sodium silicate to all geopolymer system with approximately c. 10% reduction in formation of aluminosilicate gel in all systems. Error bars are the average standard deviation from the mean value obtained from the measurement of triplicate samples.

A comparison of the degree of reaction in KW3 and KO3 systems activated only using NaOH with those using a combination of NaOH/ Na_2SiO_3 for alkali activation is shown in Figure 5.1. A reduction of c. 10% in the quantity of geopolymer gel was observed when adding Na_2SiO_3 to both systems.

Contrary to expectations, the results suggested that addition of Na_2SiO_3 had a detrimental effect on the formation of geopolymer gel. One possible explanation might be that the addition of sodium silicate reduced the setting time, which negatively affected gel formation at ambient temperatures. These results reflect those of Wang et al., (2012), Fansuri et al., (2010), and Rizwan et al., (2015) who concluded that the addition of Na_2SiO_3 in excess, led to the formation of other gel products in calcium-rich mixtures e.g. calcium silicate hydrate (CSH) gel in geopolymer systems, resulting in reduce setting time and inhibition of the formation of aluminosilicate gel (NSAH). This also accords with earlier observations reported by Giannaros et al., (2016)., which showed similar Na_2SiO_3 behaviour in cement-based systems.

To further understand these results, geopolymerisation reaction kinetics were monitored during a 28-day curing period. Figure 5.2 compares the reaction kinetics of both KW and the modified KWNS geopolymer by measuring the quantity of gel formed after 1,3,7,14 and 28-day curing.

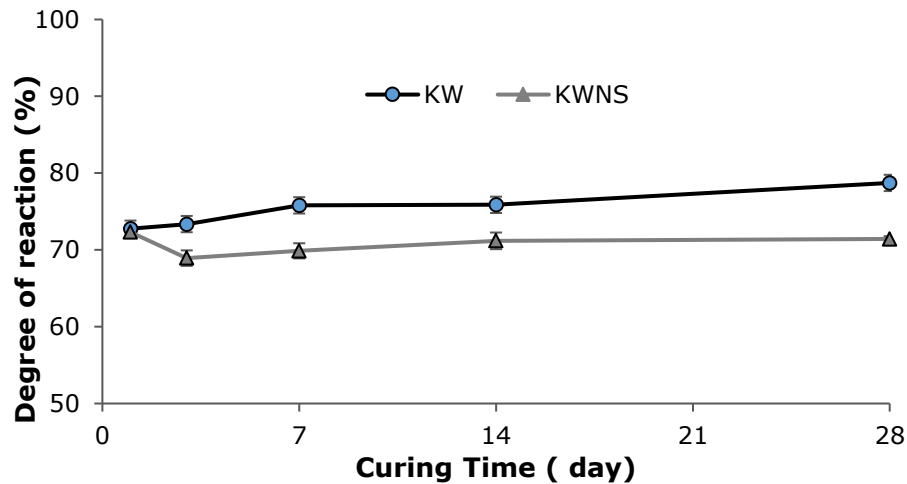


Figure 5.2: Effect of adding Na_2SiO_3 in geopolymer gel formation in KW and KWNS systems A function of time over a 28-days curing period. The Figure shows that the addition of Na_2SiO_3 to KW system (KWNS) lead to accelerate the setting time, reduce the geopolymerisation reaction rate and reduce the formation of geopolymer gel in KW system. Error bars are the average standard deviation from the mean value obtained from the measurement of triplicate samples

A positive correlation between gel formation and curing time was observed for KW (Figure 5.2) with continued gel formation over 28 days (p-value of <0.001). From the data in Figure 5.2, it is apparent that the addition of Na_2SiO_3 in KWNS system had a negative effect on gel formation with no apparent ongoing gel formation (p-value = 0.17). After 28 days the KWNS system had c. 10% less gel formation than the KW system.

Similar results were obtained for the KO and KONS systems (Figure 5.3). The increase in formation of geopolymer gel in the KO system was significant (p-value <0.001) over the curing period, where no significant change (p-value ~ 0.1) was observed in the rate of geopolymerisation reaction or gel development in KONS system following the addition of Na_2SiO_3 .

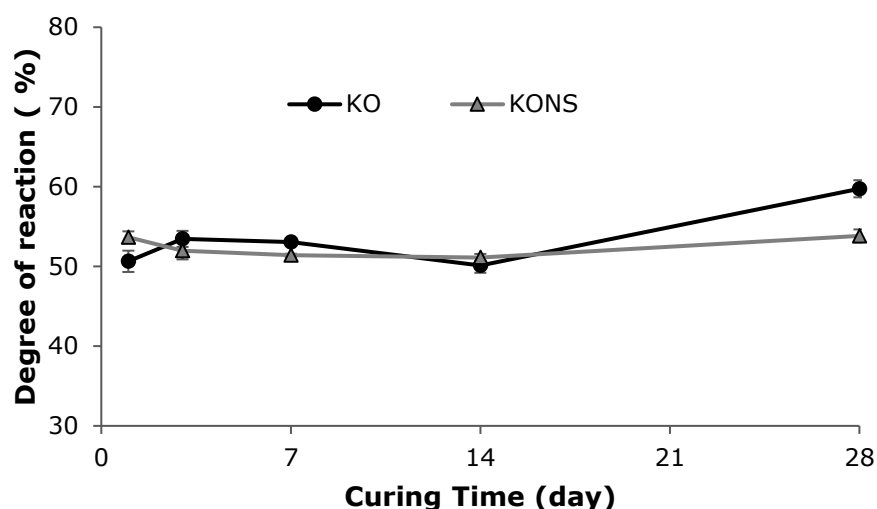


Figure 5.3: Effect of adding Na_2SiO_3 in geopolymer gel formation in KO and KONS system.

The Figure shows that the addition of Na_2SiO_3 to KO system (KONS) lead to accelerate the setting time, reduce the geopolymerisation reaction rate and reduce the formation of geopolymeric gel in KO system. Error bars are the represent standard deviation from the mean value obtained from the measurement of triplicate samples

Overall, it found that the addition of sodium silicate for both geopolymer-waste systems appeared to shorten the setting time and reduce the formation of geopolymer gel.

Further analysis was used to measure the quantity of Al and Si incorporated in gel formation during the progress of the reaction. Also, the gel content from Al and Si was used to quantify the Si: Al ($\text{SiO}_2:\text{Al}_2\text{O}_3$) mole ratio during the course of alkali activation reaction, and used to compare the effect of adding of Na_2SiO_3 in gel formation in KW and KWNS systems. Figure 5.4a shows that the rate of incorporation of Si and Al in the gel formed in KW system remain semi-constant during the geopolymerisation reaction with a mole ratio of ~ 1.1 (equivalent to $2.2 \text{ SiO}_2:\text{Al}_2\text{O}_3$) over 28-days curing period. The measurement of rate of incorporation of Si and Al in gel formation shows that both metals was reacted in equivalent rate during the course of reaction ($0.035 \text{ mol kg}^{-1} \text{ day}^{-1}$ for Si and $0.037 \text{ mol kg}^{-1} \text{ day}^{-1}$ for Al).

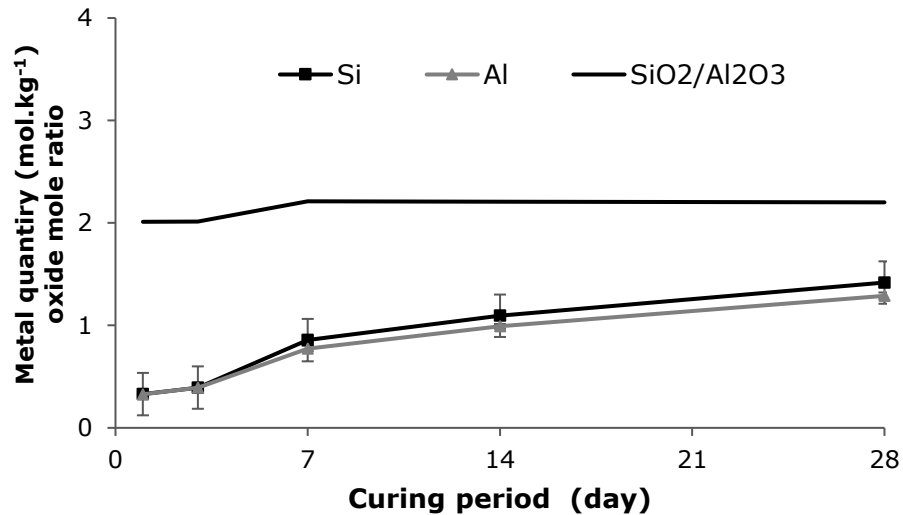


Figure 5.4a: Si: Al ($\text{SiO}_2:\text{Al}_2\text{O}_3$) mole ratio incorporated in formation of geopolymer gel in KW system. The Figure shows the rate of incorporation of Si and Al in formation of geopolymeric gel and other gels during the progress of geopolymerisation reaction within KW system. The rate of incorporation of both metals was similar during all reaction stages with approximate mole ratio Si:Al ($=1.1$) which equivalent to ($=2.2$ $\text{SiO}_2:\text{Al}_2\text{O}_3$). Error bars are the average standard deviation from the mean value obtained from the measurement of triplicate samples

Figure 5.4b compares the results obtained from measuring of Si and Al metal incorporated in formation of geopolymer gel in KWNS system at the same curing time period. The results show that the rate was declined approximately 2 times for Si ($0.016 \text{ mol.Kg}^{-1}.\text{day}^{-1}$) and 3 times for Al ($0.012 \text{ mol.Kg}^{-1}.\text{day}^{-1}$) as a result of addition of Na_2SiO_3 in KWNS system comparing with KW systems after the same curing period.

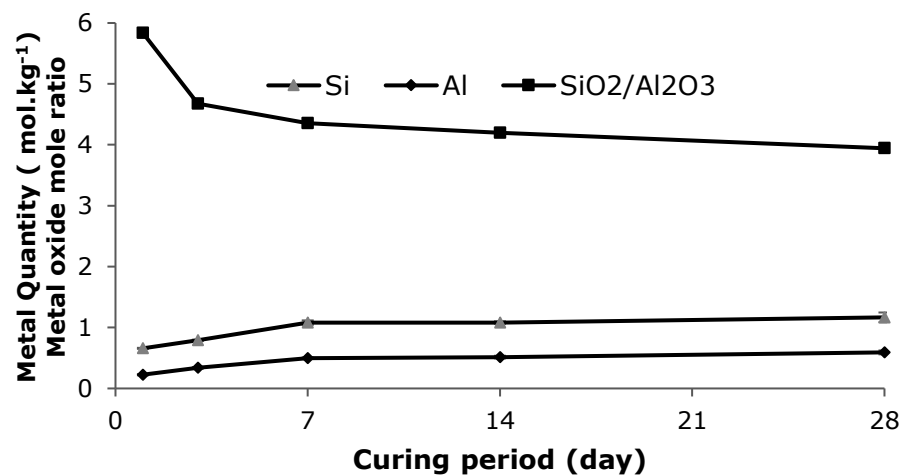


Figure 5.4b: Si: Al ($\text{SiO}_2:\text{Al}_2\text{O}_3$) mole ratio incorporated in formation of geopolymer gel in KWNS system The Figure shows that the addition of Na_2SiO_3 to KW system increase the Si: Al mole ratio to approx. (3) equivalents to ($=5.8$ $\text{SiO}_2:\text{Al}_2\text{O}_3$) in the

early stages in geopolymerisation reaction and approximately (3.94) after 28 days, which lead to reduction on the rate of incorporation of both metals and the overall $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio. Error bars are the average standard deviation from the mean value obtained from the measurement of triplicate samples.

The results also indicate that the $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio was high during the geopolymerisation of this system i.e. 3.94 after 28-days comparing with 2.2 in KW system. These results indicate that there was excess of Si during all geopolymerisation reaction stages and that addition of sodium silicate to KW system retarded the geopolymerisation process and have an adverse effect on development of geopolymer gel and the overall reaction rate.

The noticeable results were obtained in KO and KONS systems as presented in Figure 5.4c and Figure 5.4d, it is clear that the rate of incorporation of Si and Al in formation of geopolymer gel in KO was similar during the first 7 days in the curing period, the mole ratio of both metals was almost 1 as Si:Al or 2 as $\text{SiO}_2:\text{Al}_2\text{O}_3$, then increased gradually during the course of the reaction to ended up to 2 as Si:Al mole ratio or 4 as $\text{SiO}_2:\text{Al}_2\text{O}_3$ at the end of curing period.

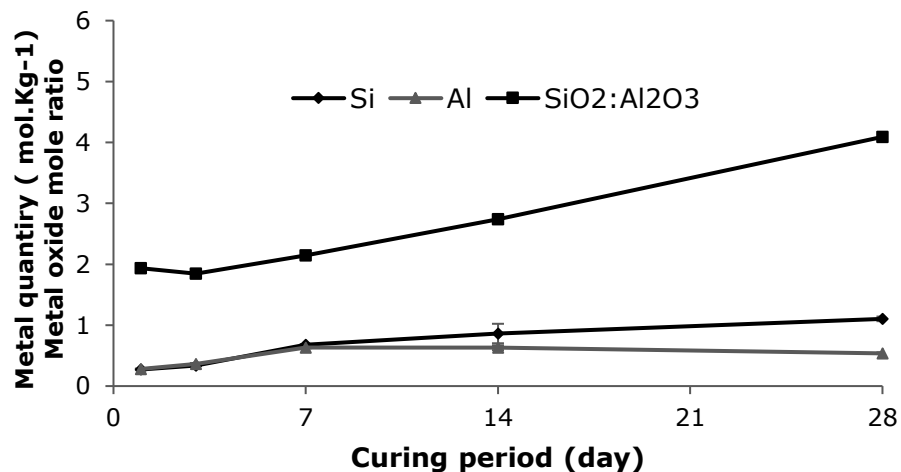


Figure 5.4c: Si: Al ($\text{SiO}_2:\text{Al}_2\text{O}_3$) mole ratio incorporated in formation of geopolymer gel in KO system. The Figure shows the rate of incorporation of Si and Al in formation of geopolymeric and other gels during the progress of geopolymerisation reaction within KO system. The rate of incorporation of both metals was different during the reaction stages. After 28 days curing, the mole ratio between Si:Al was high approximately (=2.0) which equivalent to (=4.0 $\text{SiO}_2:\text{Al}_2\text{O}_3$). Error bars are the average standard deviation from the mean value obtained from the measurement of triplicate samples

The measurement of the rate of incorporation of Si and Al metals in formation of geopolymer gel in KO system during curing procedure indicate that both metals incorporated by different rate ($0.003 \text{ mol.kg}^{-1}.\text{day}^{-1}$ for Si and $0.008 \text{ mol.kg}^{-1}.\text{day}^{-1}$ for Al metal) in this system. These results confirm the excessive existence of Si in KO system and that the $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio was increased during curing period and reached high values (4.09) after 28-days curing which indicated in many previous studies as a higher mole ratio and led to reducing the setting time of geopolymers and causing very fast compaction for the geopolymer paste resulting in the decrease of geopolymer gel formation (Silva et al., 2007; Siyal et al., 2016).

Figure 5.4d shows that addition of Na_2SiO_3 provide reactive silicates for this system and increase the rate of incorporation of Si in formation of more gel in KONS system to ($0.008 \text{ mol.kg}^{-1}.\text{day}^{-1}$), and the rate of incorporation of Al metal ($0.008 \text{ mol.kg}^{-1}.\text{day}^{-1}$). The results in Figure 5.4d show that the addition of sodium silicate to KONS system reduce the $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio in this system to 3.7 after 28 days which indicate the formation of more geopolymer gel or other gel products in this system, and led to improvement in KO geopolymer framework and the overall geopolymerisation reaction rate in this system.

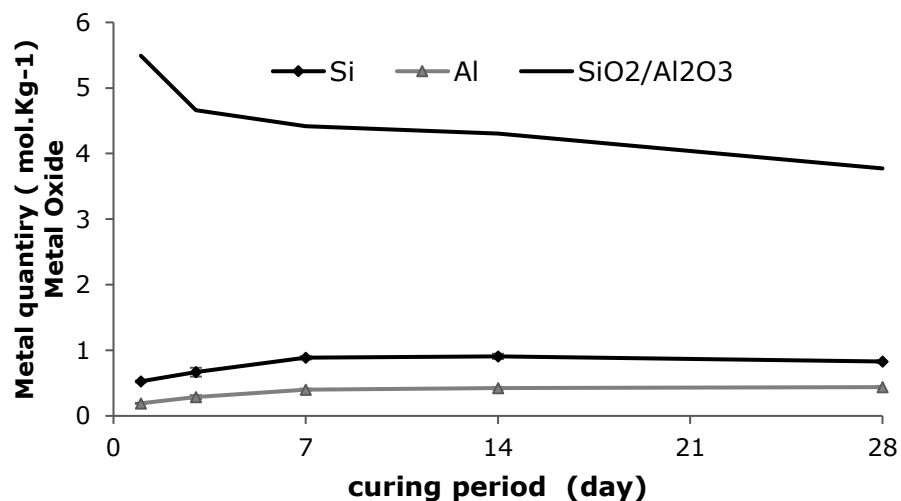


Figure 5.4d: Si: Al ($\text{SiO}_2:\text{Al}_2\text{O}_3$) mole ratio incorporated in formation of geopolymer gel in KO system. The Figure shows the rate of incorporation of Si and Al in formation of geopolymeric and other gels during the progress of geopolymerisation reaction within KONS system. Addition of Na_2SiO_3 improve the rate of incorporation of Silica and reduce

the overall $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio after 28 days curing to (3.77). Error bars are the average standard deviation from the mean value obtained from the measurement of triplicate samples

The effect of high $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio on the geopolymerisation reaction mechanism, the overall reaction rate, and on the final shape of gel geopolymer gel reported in several literature. Davidovits, (1994), Silva et al., (2005), Anseau et al., (2006) and He et al., 2012) who evaluated this effect and reported that $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio significantly determines the final structure of the resulted geopolymer materials and significantly affect the degree of geopolymerisation reaction.

In KW geopolymer system with low $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratios (≈ 2.2), and due to existence of Si and Al in similar mole ratio (≈ 1), the condensation between aluminate and silicate resulting in formation of kaolin/sodalite geopolymer framework composed mainly from poly-sialate (PS) polymer consists of SiO_4 and AlO_4 tetrahedra linked alternately by sharing all the oxygens ($-\text{O}-\text{Si}-\text{O}-\text{Al}-\text{O}-$) as reported by Davidovits, (2017). Addition of sodium silicate to KW system (in KWNS system) increased the $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio to (~ 4) leading to excessive existence of hydrolysed SiO_4 species which condense with hydrolysed aluminates, where the extra SiO_4 species condense among themselves and form oligomeric silicates forming 3D network of polymer structures poly(sialate-siloxo) (PSS) with structure ($-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-\text{O}-$) or Polysialate-disiloxo (PSDS) with structure ($-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-$).

The rate of incorporation of Si and Al in formation of geopolymer gel in KW system was faster than in KWNS system. Addition of sodium silicate to KW system reduces the rate of incorporation of Si in formation of geopolymer gel as result of excessive existence of hydrolysed silicates species which led also to slower the overall rate of geopolymerisation reaction. These results reflect those North et al., (2000). who also found that the rate of monomeric silicate with monomeric aluminate species is much more rapid than with either polymeric aluminosilicates or other silicate species.

In contrast, in KO system the $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio in geopolymer gel formed after 28 days curing was (> 4) as shown in Figure 5.4c, which according to the literature led to formation of geopolymer gel with poly(sialate-siloxo) (PSS) structure (-Si-O-Al-O-Si-O-) or Polysialate-disiloxo (PSDS) (-Si-O-Al-O-Si-O-Si-O) structure. Figure 5.4d show that the addition of sodium silicate to KO system (KONS) reduce the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio to (<3.8) which indicate that the silicate species condensed with aluminate species in this system which reflect positively in the rate of geopolymerisation reaction in this system and formation of more geopolymer gel or other gel containing silicates as CSH gel.

The results of quantifying the amount of silicates and Aluminates incorporated in formation of geopolymer gel in KW3 and KO3 geopolymer recipes, and the XRD analysis of unreacted materials remind from the acid attack for these recipes confirms existence of high quantity of unreactive silicates in form of quartz (see appendix 2).

Using the analysis data obtained by ICP-MS, the amount of reactive silicates, the actual metal oxide molar ratio and the formula of KW3 and KO3 geopolymers were recalculated based on reactive silica content, as shown below:

KW3						
			SiO ₂	Al ₂ O ₃	SiO ₂ /Al ₂ O ₃ molar ratio	
	Calculated (Reactive & unreactive)		2.7	0.8	3.4	
	Measured (reactive)		1.7	0.8	2.2	
	SiO ₂ :Al ₂ O ₃	Na ₂ O:Al ₂ O ₃	Na ₂ O:SiO ₂	Na ₂ O:CaO	CaO:SiO ₂	H ₂ O:Na ₂ O
	2.21	1.29	0.58	0.34	1.69	12.60
KO3						
			SiO ₂	Al ₂ O ₃	SiO ₂ /Al ₂ O ₃ molar ratio	
	Calculated (Reactive & unreactive)		3.2	1	3.2	
	Measured (reactive)		2.2	0.5	4.2	
	SiO ₂ :Al ₂ O ₃	Na ₂ O:Al ₂ O ₃	Na ₂ O:SiO ₂	Na ₂ O:CaO	CaO:SiO ₂	H ₂ O: Na ₂ O
	2.20	1.00	0.45	0.31	1.45	8.40

5.3.2 Effect of addition of Na_2SiO_3 on enhancement of geopolymers strength

The results of UCT are shown in Figure 5.5., it is clear that addition of Na_2SiO_3 has a destructive effect on the final strength in the KW system, but that it improved the strength of the KO system.

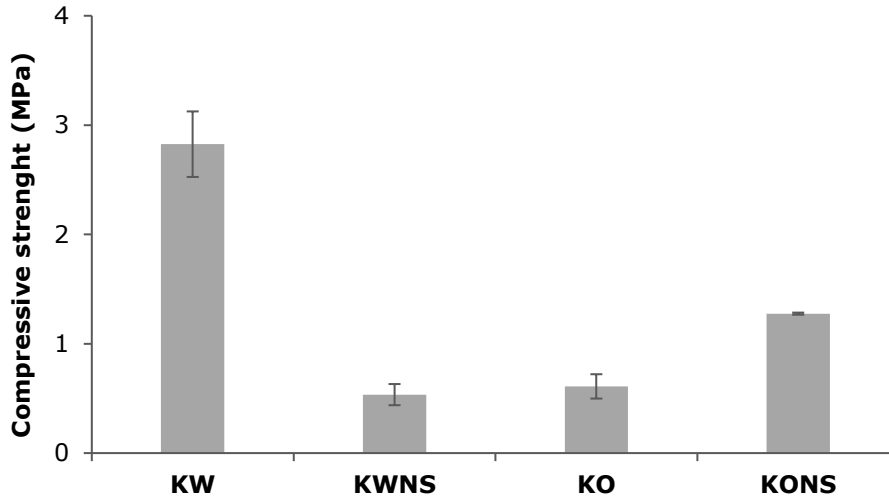


Figure 5.5: Effect of adding Na_2SiO_3 on mechanical properties of KW and KO systems. The Figure shows that the addition of Na_2SiO_3 to KW system reduce the compressive strength of this system, where show different effect on KO system by increase the strength of KONS system approx. double. Error bars represent the standard deviation from the mean for three replicates.

These results are likely to be related to the effect of $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio in the shape of final framework structures of produced geopolymer and its reflection on the internal structure properties such as porosity (size and amount) and the mechanical strength of produced geopolymer as reported by Zhuang et al., (2012). In KW system, the addition of sodium silicate lead to increase the molar ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ from 2.2 in KW system to 3.9 in KWNS system, which is higher than the optimal $\text{SiO}_2:\text{Al}_2\text{O}_3$ (3.0-3.8) recommended by many researchers (Davidivits, 2011; Kamaloo et al, 2012) to obtain geopolymers with acceptable mechanical properties. Silva et al., (2007) reported that when the $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio increases (>2), the silicate species formed as a result of the hydrolysis of SiO_2 , tend to condense among themselves to form oligomeric silicates. These oligomeric silicates in turn condense with $\text{Al}(\text{OH})_4^{4-}$, forming a rigid 3D network of polymer structures [poly(sialate-siloxo) (PSS) and poly(sialate-disiloxo) (PSDS). As a result of increasing $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio, the (PSS) and (PSDS)

framework structures illustrated in Table 1.5 become dominant in produced geopolymer gel instead of Poly-sialate (PS). PSS and PSDS have longer chains of 3d framework result in flexible, elastic behaviour in the geopolymer product, whereas shorter and smaller (PS) 3d frameworks have denser packing, and stronger reaction towards compressive loads as reported by many researchers whom conclude also that the shape of the framework within the geopolymers significantly affects the microstructure, porosity, strength characteristics and general behaviour of the geopolymer (Davidovits, 2011; Joshi et al., 2012; Chen et al., 2004).

There are, however, other possible explanations for these results, the adding of sodium silicate in excessive amounts lead to reduction on the setting time of geopolymer systems especially those rich in calcium as reported by Siyal, (2016), resulting decrease in geopolymer gel formation due to the reaction of reactive silicate with calcium and formation of CSH gel and/or calcium silicate aluminium hydrate gel (CASH) (Khater, 2013; Garcia-Lodeiro et al., 2016). The co-existence of CSH and CASH gel affects the geopolymerisation reaction and formation of sodium aluminium silicate hydrate geopolymer gel (NASH), and therefore effect the shape of final framework and mechanical strength due the formation of different structures as reported by Garcia-Lodeiro et al., (2016).

The negative impact of adding sodium silicate to mechanical properties of KW system may also attributed to the influence of this material in reduction of the setting time for geopolymer gel in KW system, resulted in prevention of evaporation of water molecules entrapped in the gel framework pores during the curing time as reported by Roviello et al., (2019), thus leading to the formation of open porosity geopolymers which substantially weakens the matrices and reduce the mechanical strength of obtained geopolymers as reported by Natali et al., (2017).

The positive effect shown in the KO system where mechanical strength was improved by c. 115 % is a consequence of reducing the $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio from 4.1 in the KO geopolymer to 3.77 in KONS system (Figures 5.4c and 5.4d) after 28 days curing period, which improves the microstructural properties and mechanical strength of this system.

These results match those observed in earlier studies conducted by Yip et al., (2005), Ridzuan et al., (2014) and Trindade et al., (2017) who found that the addition of sodium silicate to aluminosilicate materials based in kaolinite and rich in calcium activated by high concentration of sodium hydroxide produces systems containing sodium aluminate silicate hydrate geopolymeric gel (NASH), and calcium silicate hydrate gel (CSH) and that the formation of CSH gel in the early curing stages helps to bridge the gaps between the different hydrated phases and unreacted particles by the filling voids and pores within the geopolymer binder which thereby resulting increase in mechanical strength for these systems.

This finding also consistent with previous studies that have shown that Na_2SiO_3 works as a 'healing agent' for porous materials such as clay, ceramics and cement through its reaction with lime and/or calcium compounds to form calcium silicate hydrate (CSH) gel, accelerating the setting time of those systems (Giannaros et al., 2016; Gao et al., 2013; Wang et al., 2012; Rashidian et al., 2017).

5.3.3 Effect of binder particle size on improvement of geopolymer strength

The effect of the particle size on the enhancement of formation of geopolymer gel in KW and KO systems and its reflection on the improvement on geopolymer strength was investigated using compressive strength test. The effect of using kaolin binder with different particle size fractions was examined.

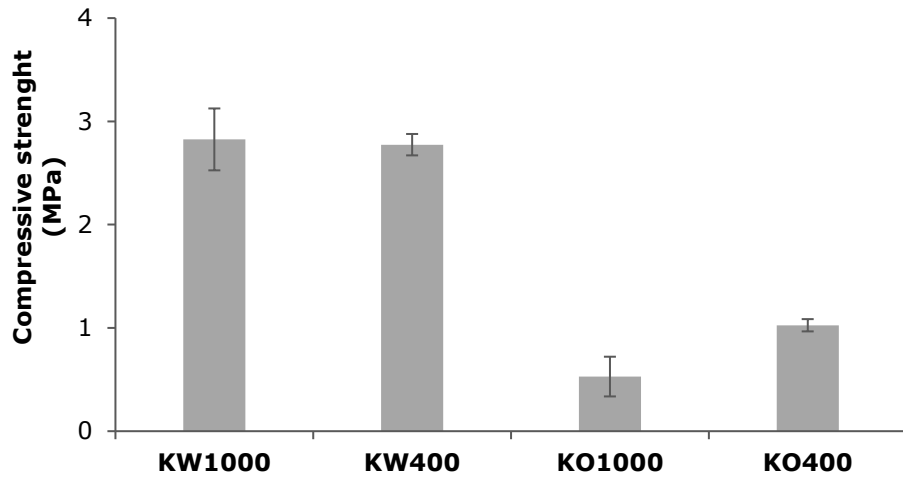


Figure 5.6: Effect of kaolin binder particle size on compressive strength of geopolymers. The Figure shows that the no-effect resulted from the addition of Na_2SiO_3 to KW system in improvement of the compressive strength of this system, where to show different effects on KO system by increasing the strength of KONS system approx. double. Error bars represent the standard deviation from the mean for three replicates.

KW1000 geopolymer system was prepared using kaolin binder has an average particle size (1000 micron) where KW400 geopolymer system was prepared with kaolin binder to have finer particle size with (<400 microns). The UC test for both systems was conducted after curing for 28-days. No significant differences were observed in improvement of the compressive strength in KW system using kaolin particle size (1000 micron) or using finer particle size (<400 micron). In contrast, using a finer particle size in the KO system gave an improvement in mechanical strength in the final material of approx. c. 100%.

The results may be explained in the basis of formation of geopolymer gel or other types of gel in both systems and the final framework structure in each system. It was believed that the lower petroleum hydrocarbons content and the lower $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio (2.2) in KW comparing with (4.09) in KO system produces the maximum amount of geopolymer gel in this system with (PS) 3d framework which have denser packing, and subsequently stronger reaction towards compressive loads. These results confirmed by the measurement of Si and Al incorporated in formation of geopolymer gel in KW system as described in Section 5.3.1 in this chapter, and the results of XRD analysis described

in Section 4.6.3 in Chapter 4, which indicate formation of sodalite phase in KW system composed mainly from poly-sialate (PS) inorganic polymer. In KW system, using of finer particle size does not exhibit any improvement in formation of more geopolymer gel or made any changes in the microstructure properties in this system.

In contrast, the higher petroleum hydrocarbon content and the high $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio (>4) in KO system expected to form lower geopolymer gel and have (PSS) and (PSDS) 3d frameworks with porous microstructure which result in formation of flexible, elastic behaviour in the geopolymer product resulted in weaker reaction towards compressive loads.

This improvement the mechanical strength in KO system may be explained by the fact that the using of finer kaolin binder size in this system significantly improved the dissolution of the aluminosilicate materials and providing enough interfacial area to silicate and aluminate species in both kaolin and drilling waste during the alkaline activation process which led to formation of more geopolymer gel or CSH gel within this system resulting in formation of more homogeneous microstructure with less porosity and reflected positively in the enhancement of the mechanical properties of this system.

This result agrees with those obtained by Christine et al, (2003), Weng et al., (2005) and Krishnaraj et al., (2018) who reported the important role of finer particle size in the dissolution of aluminosilicate materials and development of compressive strength in geopolymers.

5.3.4 Comparison between geopolymer and cement-waste systems

A comparative analysis of the physical, microstructural and mechanical characteristics of selected kaolin-waste geopolymers (KW & KO), and similar mixtures prepared using PC was undertaken. All tests were conducted in triplicate on the solidified drilling waste

after curing for 28 days in climatic conditions designed to simulate the Libyan Desert climate (Section 4.5.2, Chapter 4).

5.3.4.1 Apparent density measurements

Figure 5.7 shows the apparent density values of all selected geopolymers-waste (KW& KO), modified geopolymer (KW400, KO400, KWNS and KONS) and PC-waste systems (PCW and PCO).

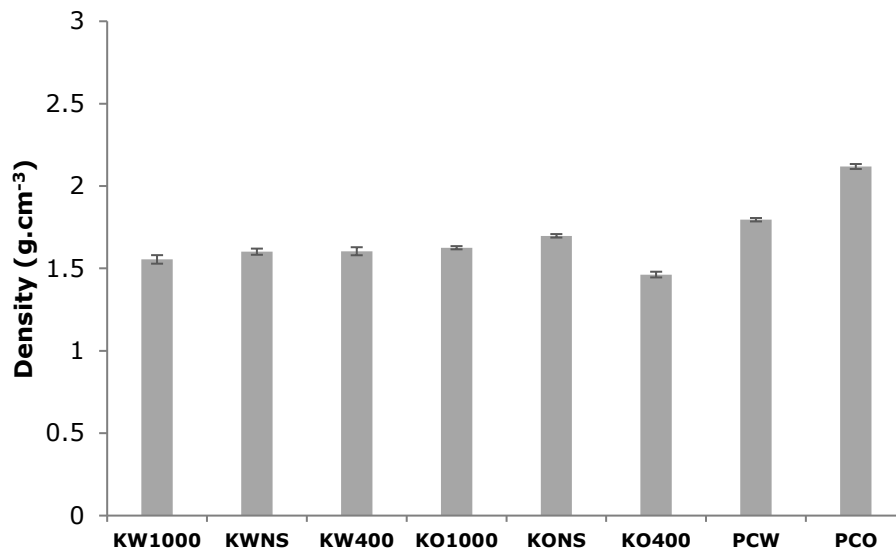


Figure 5.7: Comparison of the apparent density of KW, KW400, KWNS, KO, KO400, KONS, PCW and PCO systems. The Figure shows no observed improvement in the apparent density resulted from addition of Na_2SiO_3 or using finer particle size to KW system, where shown improvement in the apparent density resulted from addition of Na_2SiO_3 and relative reduction in the same system resulted from using finer particle size, The Figure also shown that PC-waste systems was denser than geopolymer systems, and that PCO and KO systems are denser than comparable systems PCW and KW as a result from using lower water: solid ratio Error bars represent the standard deviation from the mean for three replicates.

Overall, the results suggest that PCW and PCO systems are denser than the comparable KW and KO materials. The addition of Na_2SiO_3 or use of smaller particle size binder does not influence the apparent density of the KW system, a finding which is consistent with earlier observations in Section 5.3.3 in this chapter. By contrast, a positive influence resulted from addition of Na_2SiO_3 to KO system was observed by improving the apparent density in KONS system supporting the suggestion that the addition of reactive silicates results in an improvement in the final chemical composition and framework of the

geopolymer formed (KONS). Regardless the greater petroleum hydrocarbon content in PCO and KO systems were denser than comparable PCW and KW systems, this result may be attributed to the effect of using lower water: solid ratio in PCO and KO systems and the lower “structural water” remains as interstitial water in the both systems comparing with PCW and KW systems after completion of curing through hydration or geopolymerisation reactions as reported by Perera et al., (2006).

5.3.4.2 Water absorption and total void volume

Solidified matrixes with a higher water absorption capacity are expected to have more voids that will reflect negatively on their porous structure and mechanical strength (Blash et al., 2017). Figure 5.8 shows the percentage water absorption of solidified waste systems and compares geopolymers with materials made using OPC. It is observed that the percentage of water absorption in KW and PCW was similar and, in both cases, higher than the values obtained in KO and PO systems.

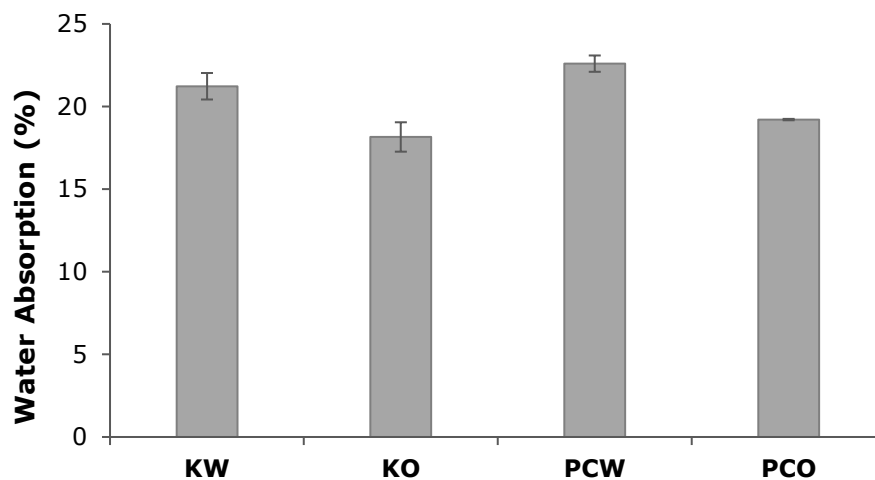


Figure 5.8: Water absorption percentage for KW, KO, PCW and PCO systems. The Figure shows that KO and PCO systems have lower water absorption percent comparing with KW and PCW systems as effect of using lower water: solid ratio. Error bars represent the standard deviation from the mean for three replicates.

A possible explanation for this might be that the lower water: solid ratio used in KO and PCO systems produces systems with fewer voids and hence porosity. The obtained result in line with the observation of Patankar et al, (2013) who concluded that water: solid ratio plays an important role in the development of the final structure of

geopolymers and PC based materials and the integrity of those systems, and should therefore be maintained as low as possible. Also, the results obtained after curing for 28-days might not provide final information about changes in the internal structure of these materials. Farhana et al, (2014) concluded that longer times were required before it was possible to judge the final microstructural properties of geopolymers.

Figure 5.9 shows that the total voids volume measured in KW and PCW is slightly greater than those for KO and PCO systems. This is consistent with the values of apparent density and percentage water absorption for the same systems. The results also confirm that the use of lower water: solid ratios in KO and PCO systems produces matrices of maximum density and lower pore void volume. In accordance with the present results, Cui and Wang, (2019) have demonstrated in previous studies that the increasing water: solid ratio contributed to the rise of the number of micro and macro pores within final geopolymer framework.

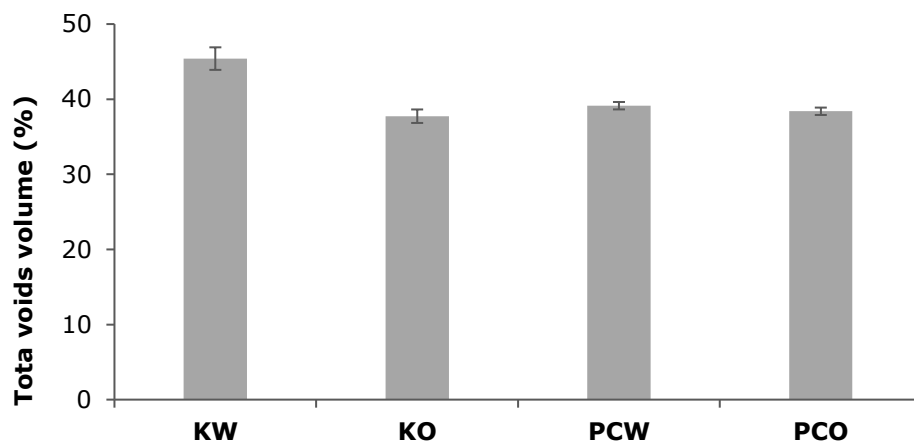


Figure 5.9: Total void volume in KW, KO, PCW and PCO systems. The Figure shows that KO and PCO systems have lower total voids volume comparing with KW and PCW systems as effect of using lower water: solid ratio. Error bars represent the standard deviation from the mean for three replicates

5.3.4 Durability evaluation of geopolymer and PC-waste systems

5.3.4.1 Ultrasonic Pulse Velocity UPV

UPV test used in this study as a non-destructive method for preliminary evaluation of the quality of KW, KO geopolymeric systems, and PCW, PCO cement concretes and compare the integrity of these systems after curing for 28 days.

Figure 5.10 shows that KW and PCW systems have higher UPV velocity and expected to have better homogeneity and higher strength than comparable KO and PCO systems. The maximum velocity and hence expected strength, was measured in PCW followed by KW, PCO, and KO respectively. The increase in velocity in KW and PCW systems reveals that they have fewer internal flaws and voids and have a better internal structure in comparison with KO and PCO where the petroleum hydrocarbon content compromises the structure unless Na_2SiO_3 is added which helps to offset this problem and produces a concrete of similar strength to that produce using PC without Na_2SiO_3 addition.

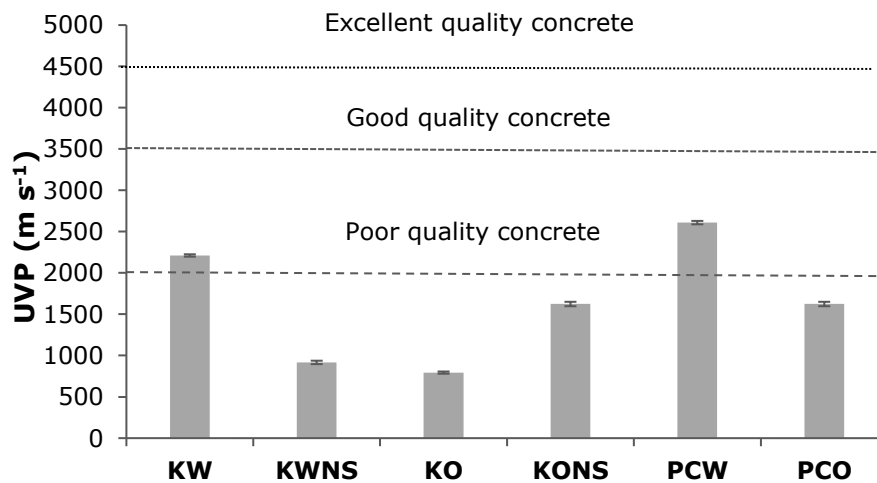


Figure 5.10: Comparison of the strength of KW, KO, PCW and PCO systems and the effect of Na_2SiO_3 addition. On mechanical properties of K-waste systems. The Figure shows that KW and PCW have better homogenise internal structure comparing with KO and PCO systems. the Figure also confirms the destructive effect of adding Na_2SiO_3 to KW system and its positive effect in improvement of homogeneity and microstructure of KO system. The Figure also compares the quality of produced S/S systems with the criteria suggested by Whitehurst (1986) to assess the quality of concrete for construction of buildings or roads. Error bars represent the standard deviation from the mean for three replicates

Although clear strength differences are observed for the different systems (Figure 5.10) all of the materials produced and cured for 28 days were of poor quality when compared to the criteria suggested by Whitehurst (1966) to assess the quality of concrete for construction of buildings or roads (Section 2.2.5, Chapter 2). However, materials KW and PCW produce solidified matrices with UPV velocities $> 2000 \text{ m s}^{-1}$ which might be expected to approach the criteria for 'good quality concrete over a more extended period to complete the curing for both systems.

5.3.4.2 Compressive strength

A comparison of compressive strengths is shown in figure 5.11. Solidified PC-waste systems had higher compressive strength than the equivalent geopolymer-waste systems with compressive strengths of 12.1 MPa for PCO and 11.4 MPa for PW compared with 2.9 MPa for KW and 0.6 MPa for KO systems. Generally, PC-waste systems had better S/S performance and produced solid matrixes with higher strength values compared with Kaolin-waste systems. The results also found that the level of contamination by petroleum hydrocarbons not affect the solidification process in PCW and PCO systems which undergoes hydration reaction, While the presence of these substances negatively affects the geopolymerisation reaction as concluded in chapter 4 section 4.6.1.3 by hardening the dissolution of aluminosilicate materials and inhibiting the formation of aluminosilicate gels and resulted poor internal structure reflects negatively on the durability behaviour of solidified geopolymer matrices. The compressive strength values revealed that addition of Na_2SiO_3 and using kaolin binder with finer particle size improves the performance and the strength of KO systems, and have counterproductive behaviour with KW systems.

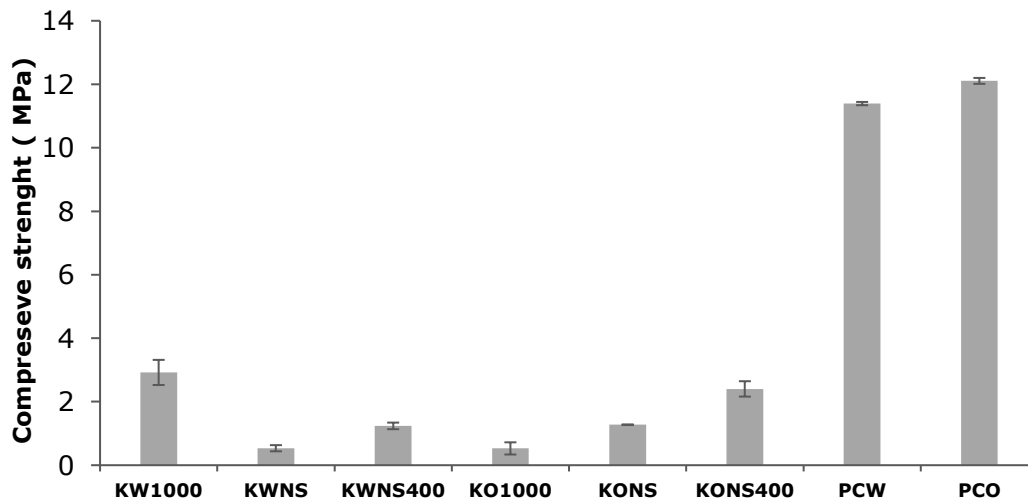


Figure 5.11: Compressive strength of solidified geopolymer and PC-waste systems. The Figure shows that destructive effect of adding Na_2SiO_3 or using finer particle size on the compressive strength of KW system. The Figure also confirms the positive effect of both factors in improvement of the strength of KO system. The Figure compares the mechanical strength of all S/S systems and shows that PC-waste systems have higher mechanical strength than geopolymer-waste systems. The obtained compressive strength values confirm the feasibility of using S/S strategy in treatment of drilling waste through deferent scenarios (safe landfill or/and recycle). Error bars represent the standard deviation from the mean for three replicates

The addition of Na_2SiO_3 improves the compressive strength of KO systems by c. 160 % compared to the corresponding KO system prepared using only NaOH. However, when added to systems with lower petroleum hydrocarbon in KW system present it appears to have a destructive effect on compressive strength compared to systems activated only by NaOH.

A finer particle size again results in a greater compressive strength for KO systems with higher hydrocarbon contents but has no effect on the KW system given equivalent compressive strength value (Figure 5.11). The combination of a small particle size kaolin binder and the addition of Na_2SiO_3 results in a substantial increase in the strength of the KO system by c. 380 % when compared with the corresponding KO system activated only by NaOH using a 1000 μm diameter kaolin binder.

These results suggest that natural kaolin clay can be successfully used without calcination as a sustainable binder to replace the use of OPC for S/S of drilling waste

containing heavy metals and petroleum hydrocarbons. Geopolymerisation at ambient Desert conditions using kaolin as a binder was able to stabilize drilling waste contains hydrocarbon contents producing a monolithic matrix with compressive strengths of up to 2.9 MPa (KW system) for waste containing up to 0.56 wt.% TOC (5600 mg kg^{-1}) and 0.6 MPa (KO system) where hydrocarbon contents were up to 3.4 wt. % TOC (34000 mg kg^{-1}). The strength of KO systems could be further improved by using a finer kaolin binder (<400 micron) to achieve 1.3 MPa or by combining both a finer particle and Na_2SiO_3 to achieve a compressive strength of 2.7 MPa.

Using OPC as a binder also had the potential to stabilize and solidify both types of drilling waste regardless of their petroleum hydrocarbon content, generating materials with greater compressive strength than the equivalent geopolymers. Although organic compounds generally interfere with the hydration reactions of cement, both PC-waste systems exhibited acceptable strength properties with PCO and PCW systems producing monolithic matrices with compressive strengths of 12.1 MPa and 11.4 MPa respectively.

There are several possible explanations for this result, firstly, the higher content of calcium oxide (quick lime) in OPC (64.5 wt. %) compared with the kaolin clay (3.4 wt. %), play very important role in encapsulation of petroleum hydrocarbon concentration. Schifano et al., (2007) and Paria and Yuet, (2007) associated the efficiency of systems that contain high amount of quick lime in reduction of petroleum hydrocarbon by the encapsulation mechanism where the petroleum hydrocarbons entrapped and fixed within the macroaggregates particles produced by the reaction of cement compounds including quicklime with water, and through the physical adsorption of hydrocarbons on the surface of cement hydration products such as CSH and CAH gels. Secondly, that OPC has a smaller particle size (<90 micron) compared to kaolin binder which help in enhance the hydration reaction and formation of CSH gel within PC-waste systems.

The results suggest that kaolin clay may be suitable for use in conversion of drilling waste into inert material or non-hazardous waste with physical properties and compressive strength adequate for various environmental management options. The wide range of compressive strengths (Figure 5.11), indicates that the solid materials could be used for suitable environmental applications in the gas or oil drilling sites in the Libyan Desert or can be more safely disposed of. For example, drilling waste containing large concentrations of petroleum hydrocarbons (KO) could be transformed to solid material using a kaolin binder and the final solidified matrix disposed of by burial close to drilling operations as a compressive strength of minimum 0.30 MPa is required for safe burial of organic hydrocarbons waste disposal practices recommended by EPA regardless of binder types (EPA report 1996).

Solidification using a finely ground kaolin binder with addition of Na_2SiO_3 (KONS400) to give strengths of c. 2.7 MPa would allow reuse as pedestrian paving. Other materials (e.g. KW) could be safely buried, or recycled for the production of other construction materials such as blocks and bricks where higher compressive strength are required (2.8 MPa, BS6073-1:1981).

5.3.5 Effect of aging on durability and leachability of geopolymer materials

To confirm the likely end-use of the materials it is however necessary to first examine how their properties change over extended exposure to the Libyan Desert climate for long aging period. In both approaches, the leaching characteristics of the treated drilling waste were compared with the UK acceptance criteria as a benchmark for leaching performance and classifying the waste as inert or hazardous waste for the safe landfill. The durability and strength performance of S/S systems was compared with the USEPA criteria for the inert waste landfill and to the British criteria for reuse/ recycle the solidified waste in the production of precast concrete masonry units.

In order to study the influence of changes in desert climate on the aging of the geopolymer and OPC formulation, 20 samples (from each system KW, KO, PCW and PCO) were prepared and exposed to the weather changes in Libyan Desert for over a 15-month period commencing in the winter of 2016. A tiny-tag data logger was placed in the shade in Jalu area located in the Libyan Desert and used to monitor temperature over the exposure period. Changes in temperature during the on-site experiment are shown in Figure 5.12.

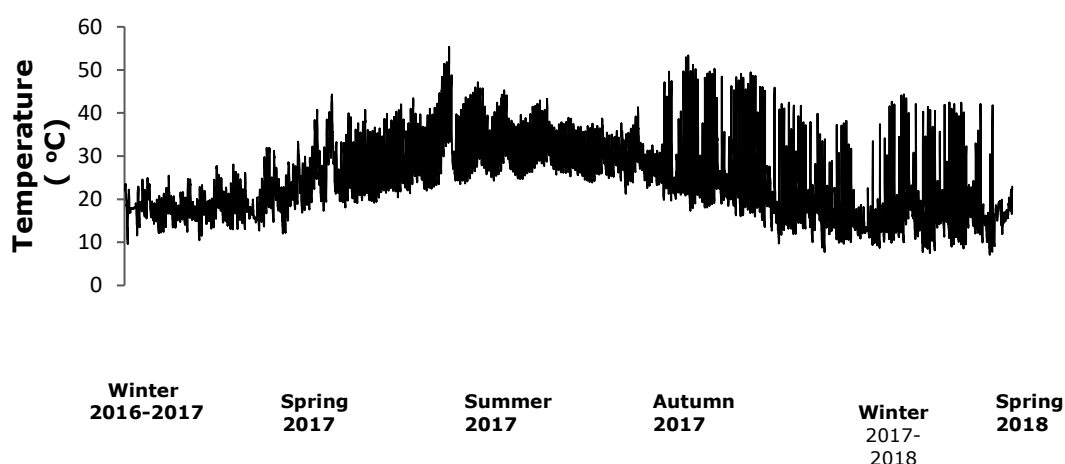


Figure 5.12: Changes in air temperature in Jalu, Libya over the 15-month period commencing winter 2016.

4 samples from each system (total of 16 sample) were returned to the university of Nottingham-UK periodically after ending of each session during the aging period and re-tested to ascertain what changed had occurred on its physical, mechanical and leachability properties due to exposure to real Desert climate over the exposure period.

5.3.5.1 Ultrasonic Pulse Velocity Test

Ultrasonic pulse velocity measurements were carried out for all system during the aging period (Figure 5.13). Increased velocities were observed in both PCW and PCO systems that had been aged. A UPV of 3557 m s^{-1} and 3400 m.s^{-1} was recorded in both PCW and PCO systems respectively indicating formation of good quality concrete according to criteria suggested by Whitehurst (1966) for quality of concrete for construction

applications shown in figure 5.13. A significant increase at the level of $p\text{-value} = 0.001$ over the exposure period recorded for both systems.

The results indicate that the quality and homogeneity of both PC-waste systems improved with aging and that both PC-waste samples have lower internal voids with aging and produce a high-density concrete that would be anticipated to have a high durability. The UVP values increased with aging and therefore continuation of the hydration reaction likely as a consequence of ongoing development of internal structure and reduction in the void volume and therefore porosity of the systems.

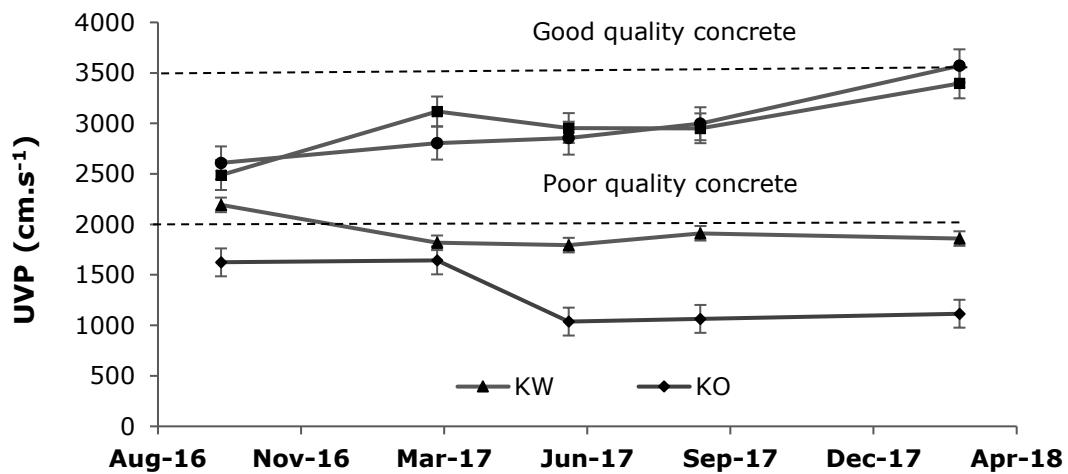


Figure 5.13: Changes of UPV of KW, KO, PCW and PCO systems and the effect of aging in Libyan Desert climate. The Figure represent improvement in UPV in PCW and PCO and indicate improvement of the quality of both PC-waste systems with aging comparing with the criteria suggested by Whitehurst (1986) for quality of concrete for construction applications. The Figure also represents changes in the quality of KW and KO systems by aging. Error bars represent the standard deviation from the mean for three replicates

In geopolymer systems, the rate and extent of enhancement in UPV was different, both systems have UPV values below 2000 m s⁻¹ indicating the poor quality of the geopolymer matrices when compared against the criteria proposed by Whitehurst (1966) for concrete quality. The UPV values recorded in the KW system decreased during the early aging period and then remained relatively constant over the aging period. The lack of change indicates that the system is completely cured and unlikely to undergo any further change. The UPV values for KO remained constant until exposed to higher

temperature during the spring and summer seasons before decreasing and remaining constant at $\sim 1000 \text{ m s}^{-1}$ for the remaining time. Completion of the geopolymerisation reaction clearly requires at least 5 months for completion, consistent with the observations and conclusions of Farhana et al (2014) that final microstructural properties and mechanical properties of geopolymers cannot be assessed over short timescales.

5.3.4.2 Compressive strength

Compressive strength changes are shown in Figure 5.14. Both PC-waste strength increased with aging. Noticeable increase (c. 100 %) over 15 months aging was recorded in PCW and PCO and appeared to be continuing beyond this.

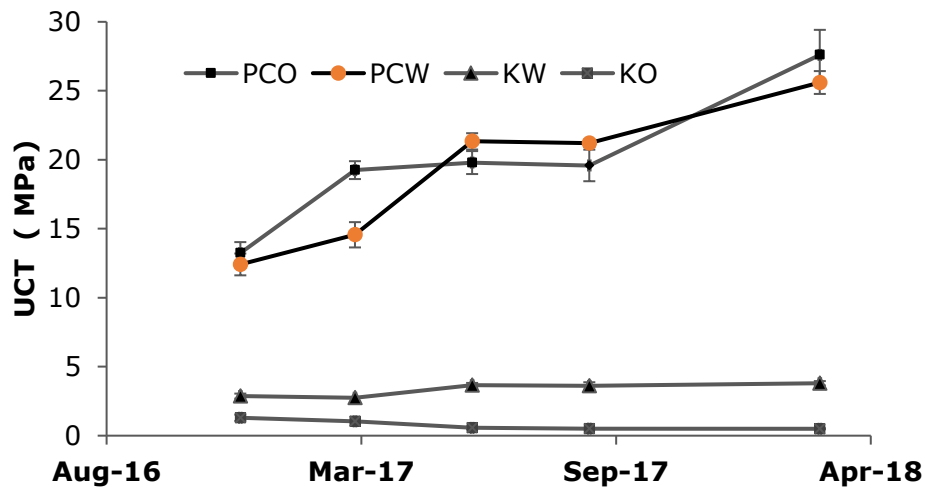


Figure 5.14: Changes in strength of KW, KO, PCW and PCO systems and the effect of aging in Libyan Desert climate. The Figure represent improvement in the strength of PCW and PCO and indicate improvement of the quality of both PC-waste systems with aging. The Figure also represents reducing in strength of KO geopolymer system in the early stages during the aging and improvement of the strength of KW with aging. Error bars represent the standard deviation from the mean for three replicates

Regarding the geopolymer-waste systems, KO system had an initially low compressive strength and this continued to decline during the early aging period then become stable with compressive strength of 0.5 MPa for the rest of aging period. Although of significantly lower compressive strength than the OPC systems the KW geopolymer gained strength during the early aging period reaching a maximum value of 3.7 MPa after aging the early six months then became stable at the same value for the rest of

aging period. This is likely to be a result of the completion of the geopolymerisation reaction and the evaporation of excess water trapped within the geopolymer network due to the increase in temperature during the spring and summer periods.

5.3.4.3 Effect of aging in leachability behavior and ability of S/S systems to causing efflorescence problem

To study the ability of solidified geopolymer-waste and PC-waste systems in reducing the efflorescence problems, and examine the effect of aging on the internal structure changes of all solidified systems, leaching procedure (TCLP) was carried to measure the quantity of uncombine salts within all S/S systems able to dissolve and leach from each system during the aging period.

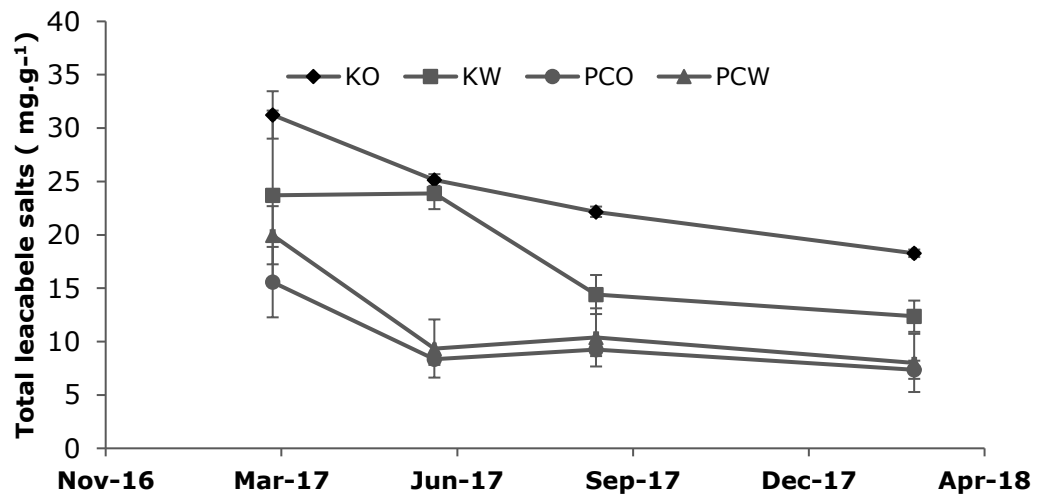


Figure 5.15: Effect of aging on the leachability of total dissolved salts from geopolymer-waste and PC-waste systems. Error bars represent the standard deviation from the mean for three replicates

Figure 5.15 reveals that there has been a gradual decrease in the level of p-value (<0.05), in the quantity of salts able to dissolve and leachate out the solidified samples and may cause formation of efflorescence compounds. The lowest ability to cause efflorescence were obtained by PC-waste systems where the concentrations of dissolved salts typically reduced up to approximately 60 % of the original concertation in PCW systems and 52% in PCO system comparing by approximately 52% in KW geopolymer and 60% in KO geopolymer system during the aging period.

The ability of leaching of salts from all S/S systems trend is contrary to the UVP and UCT measurement trend in the early and late aging stages. This trend confirms continuation of curing of PC-waste (S/S) systems and development in both microstructure and durability properties with time, where it requires more than 6 months in K-waste systems to complete the alkali activation reaction. Also, the results in figure 15.5 shown higher reduction on the quantity of salts able to leach out of all systems, which indicate incorporation of these salts in formation of more gel and improvement of microstructure properties in all solidified systems which lead to reduce the transport of salts within solidified systems during the aging period.

The lower salt leaching ability in both PC-waste systems comparing with geopolymer-waste systems is consistence with the results of improvement of mechanical strength in PCW and PCO systems with aging. Both findings may attribute to the effect of higher content of calcium oxide in PC based systems which help to form a more compact microstructure as a result of formation of more CSH gel the main product in the Portland cement (PC) hydration in these systems and lead to achieve high strength and durability as reported by Zhang et al., (2013).

The chemical analysis of the leachate indicates that most leachable species in solutions derived from geopolymer based solidified matrixes during the early aging stage are sodium ion, then the leaching of Na^+ ion was found to declines in a very significant way during the middle and late aging stages. These results reflect those of Škvara et al., (2009) who also found that the high concentration of sodium ion and the way that Na^+ ion bond with aluminosilicate materials are the main factor controls the tendency of geopolymer material to the formation of efflorescence.

Both solidified matrixes produced using the kaolin binder or with PC shown to be effective in maintaining the leaching behavior of all solidified systems not changed

adversely after a long aging period in the Libyan desert climate. The results in table 5.2 shown that all solidified samples based on geopolymers or PC converting both types of drilling waste to stable nonreactive hazardous waste (SNRHW) as classified in waste acceptance criteria proposed by the UK Environment Agency's "Waste Sampling and Testing for Disposal to Landfill" (BS EN12457-2.).

Table 5.2: Concentrations of heavy and toxic elements mobilized during aging period (mg kg^{-1}) in comparison with the UK Environment Agency's criteria proposed for classification of waste for disposal to Landfill" BS EN12457-2.

	Cr	Ni	Cu	Zn	As	Cd	Ba	Pb
<i>KW geopolymer</i>								
Oct-16	2.1	0.1	0.4	0.0	0.3	0.0	0.3	0.0
Mar-17	0.6	0.3	0.7	0.0	0.9	0.0	1.1	0.1
Jun-17	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0
Sep-17	0.3	0.2	0.6	0.0	0.4	0.0	0.3	0.0
Mar-18	0.2	0.1	0.1	0.1	0.3	0.0	1.3	0.0
<i>KO geopolymer</i>								
Oct-16	3.2	0.6	2.5	0.0	0.7	0.0	1.3	0.1
Mar-17	1.2	0.7	3.1	0.0	0.9	0.0	2.2	0.1
Jun-17	0.0	0.0	0.1	0.0	0.0	0.0	0.6	0.0
Sep-17	1.0	0.1	0.8	0.0	0.6	0.0	0.7	0.0
Mar-18	0.4	0.1	0.3	0.1	0.3	0.0	1.3	0.0
<i>PCW system</i>								
Oct-16	2.0	0.1	0.2	0.0	0.3	0.0	0.4	0.0
Mar-17	1.4	0.1	0.1	0.0	0.0	0.0	0.7	0.0
Jun-17	0.0	0.1	0.1	0.0	0.0	0.0	0.9	0.0
Sep-17	0.8	0.1	0.0	0.0	0.0	0.0	1.2	0.0
Mar-18	0.3	0.1	0.1	0.1	0.0	0.0	1.1	0.0
<i>PCO system</i>								
Oct-16	0.4	0.1	0.1	0.0	0.1	0.0	6.0	0.0
Mar-17	0.9	0.1	0.1	0.0	0.0	0.0	2.0	0.0
Jun-17	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0
Sep-17	0.6	0.1	0.0	0.0	0.0	0.0	7.2	0.1
Mar-18	0.1	0.1	0.1	0.1	0.0	0.0	6.2	0.0
<i>BS EN12457-2 criteria</i>								
Inert waste	0.5	0.4	2	4	0.5	0.04	20	0.5
Stable non-reactive	10	10	50	50	2	1	100	10
Hazardous waste	70	40	8.	200	25	5	300	50

It is clear from Table 5.2 that the heavy metal leachate from all solidified samples was lower than those of listed in the BS EN 12457 regulation. to classify the treated drilling waste as stable nonreactive hazardous waste (SNRHW) accepted at non-hazardous landfills.

Arsenic, Cd, Cu, Zn, Ba and Pb were successfully immobilized in the geopolymer network and cement systems. After more than 1 year of aging the quantity of most heavy and toxic metals in the leachate of solidified samples remain almost have the same in both solidified systems, This indicates that the hydration products within PC-waste systems managed to stabilise the HMs through chemical fixation or physical adsorption and/or encapsulation of the contaminants in the surface of hydration products in cement based systems according to the mechanism proposed by Vu and Gowripalan, (2018), or through capturing the HMs within the geopolymers framework through the bonding to the geopolymer structure, or through the physical encapsulation within the geopolymer matrix as proposed by Davidovits (1994) . The results may be used as proof of the completion of curing procedures for both system and to confirm the stability of both systems under different Desert climate condition and low permeability properties they have.

5.3.4.4 Encapsulation of petroleum hydrocarbons

The results obtained from study the effect of aging on the leachability behaviour of petroleum hydrocarbons of all solidified systems presented in table 5.3. The concentrations of petroleum hydrocarbon fractions, F2 (C10-C16), and F3 (C16-C34) were measured in the leachate over intervals during the 1-year aging period the GC-FID chromatograms results for raw materials and the leachate of PC and geopolymer bases (S/S) systems included in appendix 4.

The results show that all S/S systems maintain a high retention efficiency of petroleum hydrocarbons during the aging period. The changes in the TPH concentration during the aging period was very limited. The maximum concentration of TPH in the leachate of all geopolymer and PC based S/S systems during the aging period was within the criteria for granular waste acceptable at landfills proposed by the UK Environment protection agency.

The results (Table 5.3) also broadly support the results and observations emerged from studying the effect of aging on strength and leachability behavior of all solidified systems and confirms the improvement of microstructural properties and leachability behavior with aging and the completion of transformation of raw materials in all systems to gels, and transformation of drilling waste from hazardous waste to stable non-reactive hazardous.

Table 5.3: TPH concentration in leachate of S/S systems during aging period (mg kg^{-1}) in comparison with the UK Environment Agency's criteria proposed classification of waste for disposal to Landfill" BS EN12457-2.

Aging Period	KW	KO	PCW	PCO
	TPH conc. in leachate (mg kg^{-1})			
Oct-16	102	47.2	30.5	36.7
Mar-17	105	47.9	31.3	37.8
Jun-17	33.4	66.9	39.4	62.4
Mar-18	31.0	43.7	37.3	223
<i>Criteria for granular waste acceptable at landfills</i>				
Inert waste			500	
Stable non-reactive				
Hazardous waste			800	
Hazardous Waste			1000	

The reduction of leachability of hydrocarbons in geopolymer and PC based (S/S) system may attribute to the encapsulation mechanism and the stability of new phases produced within Kaolin-waste geopolymers or PC-waste systems, where the petroleum hydrocarbons trapped within the frameworks of CSH, CASH and NASH phases resulted from alkali activation of kaolin-waste systems, and CSH phases formed by hydration of PC-waste systems. The co-existence of hydrosodalite, katoite phases within kaolin/zeolite and calcium-based geopolymer gel (S/S) exhibits a mesoporous structure with very low pore size, high surface area and excellent adsorption capacity for petroleum hydrocarbon in geopolymer based (S/S) systems as reported by Bandura et al., (2017). In (S/S) PC based systems- it believed that the petroleum hydrocarbon encapsulated within the hydration reaction products CSH (calcium silicates C3S and larnite C2S) and portlandite (shown in XRD results (appendix 2) as concluded by Schiano and Thurston, (2010).

5.4 Conclusions

The first objective of the current study was to investigate the effect of addition of sodium silicate on the formation of geopolymer gel, improvement of the microstructural and strength properties of selected geopolymer recipes, as well as the effect of using a finer kaolin binder particle size. The main results drawn from obtained finding and discussion can be summarised as follows:

- In general, the results confirm the finding and conclusions of Chapter 4, regarding the selection KW3 and KO3 geopolymer systems as the optimum recipes that form the greatest amount of geopolymer gel, with better microstructure. These recipes also typically achieve the required leachability criteria.
- The addition of sodium silicate to the KW system retard the geopolymerisation reaction in this system by slowing the rate of formation of geopolymer gel and increasing the $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio in the gel to 4, leading to formation of longer chains within the frameworks, forming more pores and voids and negatively impacting the porosity, mechanical strength of this system. No evidence was found to support the using of finer particle size from kaolin binder to enhance of the reactivity in the KW system or improve geopolymer gel formation.
- The most important finding was the significant positive effect of adding either Na_2SiO_3 or a kaolin binder with finer particle size (<400 microns) on the performance of the KO3 system. The addition of Na_2SiO_3 encourage the formation of geopolymer gel and also worked as a healing agent and filler improving the poor microstructure of the KO3 system. This resulted in improved porosity and smaller pore size which reflected positively on both leaching and mechanical characteristics. The use of a finer particle size kaolin binder enhanced the reactivity of aluminosilicate materials in this system and positively affected the final strength. Addition of both Na_2SiO_3 and the use of the

finer particle size binder improved the microstructural properties of KO3 system and increased its final strength by approximately four times.

- Natural kaolin clay was effective for the conversion of the drilling waste into an inert material with physical and compressive strength properties adequate for various waste disposal options, providing a sustainable and cost-effective approach to treatment of treatment of the toxic waste generated during exploration and production of oil and gas.

Overall, these results support the hypothesis of this study regarding the possibility of reuse of treated drilling waste in selected construction applications in the place of waste generation. Based on their compressive strength values of geopolymer- waste systems KW3 and KO3 the final geopolymer-waste solidified matrices could be safely disposed of in a properly selected burial sites close to drilling operations sites, or solidified using kaolin binders of particle size <400 micron and Na_2SiO_3 (KONS400 recipe) to allow reuse as pedestrian paving or for other construction application not requiring materials of high compressive strength.

Solidified matrixes produced by the KW recipe and waste of lower petroleum hydrocarbon content (c.0.59 wt. %) could be safely buried, used in ground improvement works on site or recycled as aggregate for the production of construction materials such as blocks and bricks where a higher compressive strength is required. Comparison to drilling waste solidified using OPC shows that the geopolymers have poor microstructures and strength. In part this may be due to the higher content of CaO in OPC and its very fine particle size resulting in solidified matrixes with better internal structure and higher mechanical strength.

The second objective in this study was to establish the effect of Desert climate on the performance of geopolymer-waste systems (KW and KO) and determine what changes

in physical, mechanical properties and leachability occurred during aging for 1 year. The main conclusions were;

- That solidified geopolymer-waste and PC-waste systems were not substantially affected by the climatic changes resulting from exposure in the Libyan Desert. Physical, mechanical and leachability behavior remained relatively unchanged. These indicate the stability of all (S/S) systems. The only minor effect was recorded in the KO system during the first 90 days where a decline in mechanical strength was observed despite this it still had sufficient mechanical strength to enable its disposal safely by burial.
- PC-waste and KW systems both gained strength during the one-year period of aging. The strength of PC-waste system approximately doubled, where the strength of KW geopolymer-waste system increased by approximately 1.5 times.
- The improvement in the internal structure of solidified-waste systems and geopolymer -waste systems reflected positively on the leachability of those systems during aging. The amount of dissolved salts in PC-waste systems typically reduced by up to 60 % of their original concentration, and the reduction in geopolymer-waste systems was c.50% over the same time period.
- The results confirm that longer times are needed for development of the physical properties and strength of both geopolymer-waste and PC-waste matrices. A time of 28 days was not enough to judge the final properties of either system and longer curing times are needed for a proper examination and evaluation of their efficiency.

The findings of this research also support the observations and conclusions of previous studies related to the effect of metal oxide ratio ($\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$), ($\text{SiO}_2 : \text{Al}_2\text{O}_3$), ($\text{H}_2\text{O} : \text{Na}_2\text{O}$) and the effect of addition of Na_2SiO_3 and particle size on the physical and

mechanical properties of geopolymers and the effect of curing time to judge the actual physical, mechanical and leachability properties of geopolymers. These research results can be used as ground information for further studies to improve the performance of Kaolin-waste geopolymers and its durability using lower water: solid ratio or by adding of adsorbent materials and filler to enhance the microstructure properties.

Chapter 6: Assessment of Bermuda grass (*Cynodon dactylon*) for the Phytoremediation of oil industry drilling waste

6.1 Introduction

The production of oil and gas involves the generation of drilling waste, a major source of pollution in the oil-producing environment (Onwukwe and Nwakaudu, 2011). In Libya, drilling and exploration companies discharge these waste materials overboard in offshore operations or transport them to onshore utilities for treatment or disposal. Onshore drilling operations store the drilling waste in earthen pits close to drilling operations before disposal to the land or buried in the pits. The drilling waste generation, transportation, and storage activities have the potential to impact negatively on the environment polluting of water bodies, land, and the air.

The selection of a disposal method for a given location will depend on a wide range of factors that must be extensively evaluated before implementation. Temporary storage in pits close to drilling operations without treatment is the most common approach for onshore sites. This is simple and low-cost but is unsuitable solution for wastes that contain high concentrations of organic materials, heavy metals or other harmful components that could migrate from the pit to cause pollution of surrounding water bodies, soil and air (Biltayib, 2006).

The selection of the remediation strategy is usually a balance between the cost of the treatment, availability of infrastructure and the time required for remediation. Traditional treatment approaches for the management of drilling waste include land application, underground injection, thermal techniques and biological remediation techniques (Onwukwe and Nwakaudu, 2012). At the present time in Libya, and similarly in most developing countries, there are challenges that prevent the use of physical and thermal disposal techniques. The main contraindications are the severe lack of appropriate infrastructure and the technical experience needed for management and disposal in this way (Ehmiad, 2008).

Biological treatment solutions such as bioremediation have become valuable alternatives to chemical and physical (traditional) methods. Bioremediation works to either 'decontaminate' the polluted soil or to 'stabilise' the contaminants within the soil (Cunningham et al. 1995). Bioremediation is considered one of the simplest and lowest-cost techniques, as its cost is 60–80% lower than physicochemical treatments (EPA 2006; Tangahu et al., (2011)), since it does not require expensive equipment or highly specialized personnel. The bioremediation treatment technique is cost-effective for large volumes of water having low concentrations of contaminants and for large areas of surface soils contaminated by low to moderately levels of heavy metals or hydrocarbons as suggested by Ifon et al., (2019).

Bioremediation treatment techniques divide into two broad categories: *in-situ* and *ex-situ* (US EPA, 2018). Amongst bioremediation techniques, phytoremediation has emerged as a good *in-situ* choice to detoxify polluted sites (soils, water, and sediments) and is considered a 'clean' technology as no external power source is required.

Phytoremediation involves the use of vegetation to remove and control wastes, or to augment waste break down through the action of microorganisms present in the plant's rhizosphere through phytotransformation, rhizosphere bioremediation, Phytostabilisation, phytoextraction, phytovolatilization or rhizofiltration (McCutcheon et al., 2003). It therefore has the potential to minimise the concentration, mobility and toxicity of contaminants in contaminated media (Wuana and Okieimen, 2011). The most important factors affecting the success of phytoremediation and the time required to remediate contaminated soils are plant type and the addition of soil amendments and/or bulking agents (Rhykerd et al., 1999; El-Dars et al., 2016; Shrestha et al., 2019).

Phytoremediation is most effective at sites where contamination by organic materials or heavy metals is not too substantial. Among the various mechanisms involved in

phytoremediation of contaminated soils, Rhizodegradation is of greatest importance for the removal of hydrocarbons from soil (Asim et al., 2015; Dhote et al., 2017).

Rhizodegradation is enhanced by the presence of plant root exudates including enzymes and flavonoids, organic acids, sugars and amino acids, which play an important role in inducing the growth of bacteria and fungi in the rhizosphere leading to degradation and mineralization of hydrocarbons pollutants (Reichenauer and Germida, 2008; Dadrasnia and Ismail, 2015).

Several plants have already been identified and trialled for rhizoremediation of organic compounds and heavy metals, including wild grass species such as Bermuda grass (*Cynodond actylon*), tall fescue (*Festucaarundinacea Schreb*), and star grass (*Ponterderiaceae*) (Izinyon et al., 2013; Tsao, 2003; Yin et al., 2013; Anyasi and Atagana, 2018). All of mentioned grasses have fibrous root systems, resulting in large root length and surface area per unit volume of surface soil, the fibrous roots provide a larger surface area for colonization by microorganisms than a taproot plant, allow greater interaction between rhizosphere microbial community and the contaminant. During rhizoremediation, uptake and degradation rate of organic compounds are restricted by the hydrophobic and toxic nature of the contaminants, as well as the synergy existing between plant roots and soil microorganisms (Wang et al., 2011).

Bermuda grass a widely used as warm season turfgrass (Shi et al., 2012), and considered as one of the most tolerant grasses to drought, anoxia, and high salt content soils. Bermudagrass species grow well on a variety of soil types ranging from heavy clay to deep sands, it is also tolerating both acid and alkaline soil conditions salt, cold and soil compaction (Gamble and Rhoads, 1964; Turgeon, 1980; Beard, 1988; Buble, 2009). Moreover, it has extensive, fibrous, widely branched and deep root systems that can provide a large root surface area for colonization by rhizosphere microorganism (Turgeon, 1980).

Bermuda grass is widely used as warm season turfgrass (Shi et al., 2012), and considered as one of the most tolerant grasses to drought, anoxia, and high salt content soils. Bermudagrass species grow well on a variety of soil types ranging from heavy clay to deep sands, it is also tolerating both acid and alkaline soil conditions salt, cold and soil compaction (Gamble and Rhoads, 1964; Turgeon, 1980; Beard, 1988; Buble, 2009). Moreover, it has extensive, fibrous, widely branched and deep root systems that can provide a large root surface area for colonization by rhizosphere microorganism (Turgeon, 1980).

The main objective of this research was therefore to assess the ability of Bermuda grass to grow in soil contaminated by drilling waste contains petroleum hydrocarbons and heavy metals, and to consider the feasibility of adoption of this species in Libya for phytoremediation of drilling waste and stabilisation of contaminated soils.

6.2 Material and Methods

6.2.1 Materials

Two different drilling waste samples and a sample of uncontaminated 'native' soil were collected during drilling operations in the Jalu area of the Libyan Desert as described in Section 2.1.1, Chapter 2. All samples were dried in air for 2 weeks, sieved through 2 mm mesh to eliminate coarse rock and plant material, and thoroughly mixed to ensure uniformity.

Bermuda grass (*Cynodonta ctylon*) was selected as the plant species due to its ability to grow in the harsh conditions of temperature, light and drought experienced in the Libyan Desert.

Composite fertilizer NPK with ratios of N: P₂O₅: K₂O of 10: 8: 9 was prepared from high purity potassium nitrate and phosphate salts (Fisher Scientific UK).

6.2.2 Green House Experiments

Pot experiments were conducted in a greenhouse at the School of Bioscience, University of Nottingham during the summer period (June, July, and August) in order to grow grass in conditions as similar as possible to the Libyan Desert for 60 days. The experimental design utilized three different soils; control (C, native uncontaminated soil), WBM (W, soil contaminated with water-based drilling waste), and OBM (O, soil contaminated with oil-based drilling waste). Different proportions of native added to the contaminated soil (300 g in total) using different dilution factors shown in table 6.1 was added to plastic pots with radius 7 cm and height 15 cm (Table 6.1). Each treatment was replicated 4 times, giving a total of 28 pots.

Table 6.1: Description of pot experiment design.

Code	Treatment	Dilution Factor	TOC wt. %	Approx. TOC concentration mg kg ⁻¹
C	Control (Native Soil)	1	0.15	150
25-W	25 WBMW:75 Native Soil	4	0.37	3675
50-W	50 WBMW:50 Native Soil	2	0.74	7350
100-W	100 WBMW	1	1.47	14700
25-O	25 OBMW:75 Native Soil	4	2.14	21400
50-O	50 OBMW:50 Native Soil	2	4.28	42800
100-O	100 OBMW	1	8.56	85600

According to preliminary tests, the optimum germination rate of Bermuda grass in native soil required seeding at a rate of 50 g m². Seeds were sown at this rate and the pots arranged in randomized complete block design in the greenhouse for 60 days. During this time the temperature ranged between 25 to 35°C, and humidity between 40-60%. lighting was natural sunlight with a light/dark cycle of approximately 16/8 hr.

Irrigation water was added to achieve 30% of the water holding capacity of each treatment (c. 0.1 ml g⁻¹) to avoid leaching of hydrocarbons and heavy metals. In addition, pots were supplied with a liquid compound fertilizer supplying essential nutrients (ratio of N: P₂O₅: K₂O of 10: 8: 9) weekly. After 60 days, the plants were carefully extracted from each pot and divided into roots and shoots. Both parts were placed sealed in plastic bags and stored in a cool place until analysis.

6.2.3 Analysis

Fresh shoot weight was measured at harvest along with shoot length. Leaf area was also measured as described Section 2.3.2.5, Chapter 2. Shoots were then freeze dried to avoid loss of volatile petroleum hydrocarbons, milled and stored in a plastic tube prior to analysis. Sub samples were digested and analysed for heavy metals using ICP-MS as described in Section 2.3.2.2, Chapter 2. The roots were washed thoroughly with tap water then with deionized water to remove soil particles, root length measured, and then samples were placed in paper bags and dried in an oven at 45 °C for 72 hours until a constant weight was achieved and the dry-weight of biomass was determined.

Due to the potential contamination of plant shoots by soil dust, which result in obtaining high concentrations values of metals in the shoots samples, leads to incorrect interpretation of the results, and affects the actual evaluation of the capability of bermudagrass in metal uptake, the proportion of metal in plant samples originating from contaminant soil (P_{metal}) was estimated using the following equation suggested by Joy et al , (2015), and used to estimate the actual concentration of metal in plants which has been acquired from the soil via uptake through the root system and transfer into the plant shoots.:

$$P_{metal} = \frac{V_{plant} \cdot Metal_{soil}}{V_{soil} \cdot Metal_{plant}}$$

Where V_{plant} and M_{plant} are elemental concentrations in the plant, and V_{soil} and M_{soil} are concentrations in the soil.

The capability of Bermuda grass to extract the HMs from the soil to shoots at harvest estimated by calculation of transfer factor (TF) according to the following formula (White et al., 2005).:

$$Transfer\ factor\ (TF) = \frac{M_{shoots}}{M_{soil}}$$

Where M_{shoots} = concentration of HMs in shoots

M_{soil} = concentration of HMs in soil

Transfer Factors >1 means the most of heavy metal are accumulated in the shoots, The petroleum hydrocarbons in the in planted and unplanted treatments was extracted for TPH analysis using solvent extraction before GC-FID analysis (Section 2.3.2.1, Chapter 2) conducted. Petroleum hydrocarbons were extracted from the soils, using high purity reagent grade dichloromethane as solvent and anhydrous sodium sulphate (Fisher Scientific, UK). A high purity C8-C40 alkanes calibration standard in dichloromethane (Sigma-Aldrich) was used for the calibration of GC-FID.

Soils microbial activity in the rhizosphere was evaluated using Biolog plates and the activity of the microbial enzyme was evaluated by measuring the DHA as described in Sections 2.4.2.6 and 2.4.2.7 of chapter 2.

6.3 Results and Discussion

6.3.1 Soil and waste analysis

The physical, chemical and textural analysis of the soil and drilling waste contaminated soil prior to the experiment is given in table 6.2. Samples have a sandy loam texture and are classified as calcareous soil with a negligible nutrient content (N, P). Both waste samples have high petroleum hydrocarbon content and are considered hazardous waste when compared the UK landfill acceptance criteria for granular waste acceptable at landfills (Appendix 1). The main elemental contaminants were As, Cd, Co, Mo, V, Pb, Cu, Zn, Ni, and Cr. The heavy metals content (with the exception of Zn in WBM) are in compliance with the upper limits allowed for dispose to landfill in the UK (EBPRI 11507B (2013)).

Table 6.2: Physical properties, chemical composition and texture of soil samples

Test	Unit	WBM	OBM	Native Soil
pH	-	8.4	8.8	8.7
EC	mS cm ⁻¹	4.06	4.2	0.08
T.D.S	mg kg ⁻¹	2035	1995	38
Moisture	Wt. %	12.4	55.2	3.79
L.O.I	Wt. %	21.3	59.5	4.35
TOC	Wt. %	1.47	8.56	0.015
Cr	mg kg ⁻¹	28.4	34.3	10.8
Mn	mg kg ⁻¹	43.3	33.7	80.1
Cu	mg kg ⁻¹	9.3	34.5	16.4
Zn	mg kg ⁻¹	50.9	74.8	19.3
As	mg kg ⁻¹	2.0	6.17	1.37
Cd	mg kg ⁻¹	0.44	0.72	0.0
Ba	mg kg ⁻¹	1066	3832	242
Pb	mg kg ⁻¹	10.3	61.0	7.07
Na	mg kg ⁻¹	2089	2217	1328
Ca	mg kg ⁻¹	280972	253821	5978
Mg	mg kg ⁻¹	2211	19523	1843
K	mg kg ⁻¹	1279	11306	7218
Cl	mg kg ⁻¹	8400	6590	112
NO ₃ -N	mg kg ⁻¹	0	0	0
PO ₄ -P	mg kg ⁻¹	0	0	0
SO ₄ ²⁻ -S	mg kg ⁻¹	303	2152	120
Mean Particle Size	µm	314	193	124
Specific Surface Area	cm ² g ⁻¹	2043	3173	795
Soil Texture	-	Loamy Sand	Loamy Sand	Sand
		Calcite (CaCO ₃)	Calcite (CaCO ₃)	Quartz (SiO ₂)
Mineralogy		Quartz (SiO ₂)	Quartz (SiO ₂)	
		Ankerite (Ca(Fe,Mg)(CO ₃) ₂)	Baryte (BaSO ₄)	

6.3.2 Growth, leaf area and biomass measurements

Attempts to grow the grass in the OBM were unsuccessful even in mixtures containing 75% uncontaminated soil (25-O) thus these systems will not be considered further. Bermuda grass did however show a promising ability to grow in soils contaminated by water-based drilling waste and low to medium levels of TPH and HMs (Figure 6.1). Growth in control samples and mixtures containing up to 50% WBM and 0.74 wt % TOC (25-W and 50-W treatments) was similar over 60 days. No visible adverse symptoms such as wilting, lodging or defoliation was observed. No significant difference in biomass was observed between the control and the 25-W treatment ($p > 0.1$), but significant ($p < 0.001$) reductions in biomass were observed in both the 50-W and 100-W treatments (Figure 6.2). Grass growth in the 100% WBM contaminated soil (100-W) was by comparison severely stunted (Figure 6.1) with a substantial decrease in both biomass (Figure 6.2) and grass height (Figure 6.3).

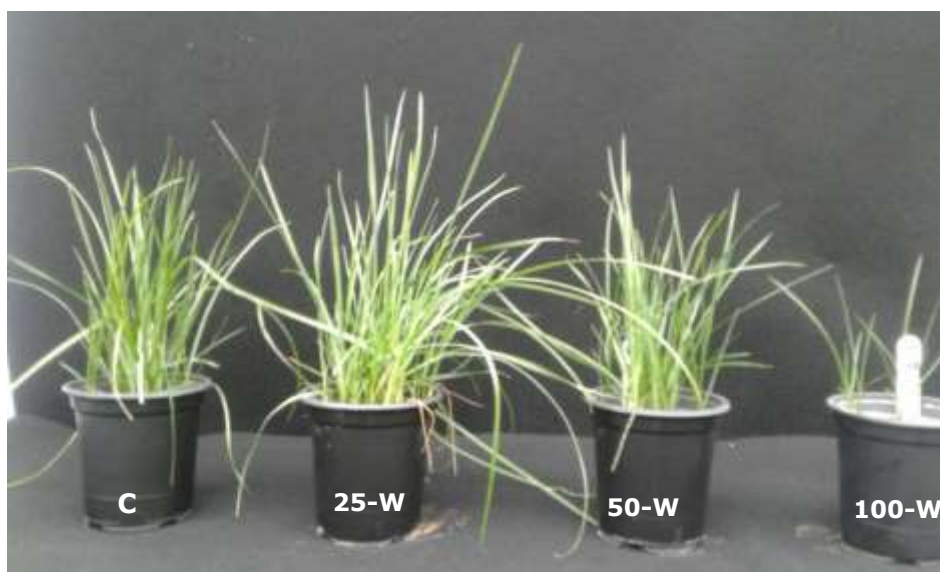


Figure 6.1: Variation in Bermuda grass growth over 60 days in soils containing 25, 50 and 100% water-based drilling waste. The Figure shows the destructive effect of TPH on the biomass of the areal parts of Bermuda grass planted in different TPH contamination level. No differences observed between the control and 25-W treatment. The reduction in biomass increases as the contamination by TPH increases.

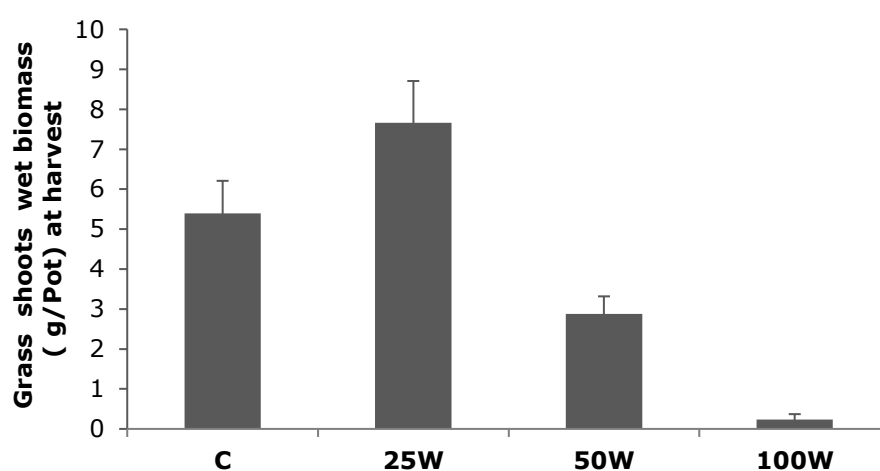


Figure 6.2: Total biomass (wet weight) of Bermuda grass grown in soils with increasing proportions (0, 25, 50 and 100%) of water-based drilling waste (WBM) at harvest. The Figure shown that the biomass of the aerial parts reduced with increasing the soil contamination level by petroleum hydrocarbons. Error bars represents the standard deviation from the mean value for triplicate samples.

Overall plant height decreased significantly with increasing contamination level ($p < 0.001$) however no difference in average grass height was observed between control and 25-W, with an average height of ~ 29 cm achieved in both treatments

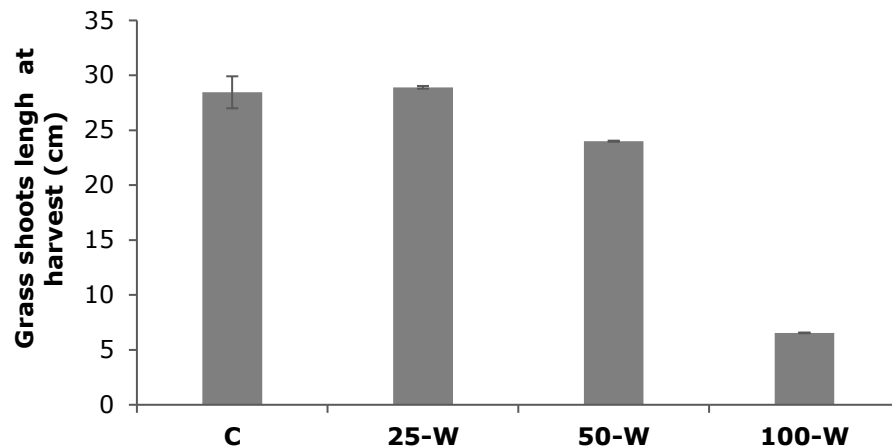


Figure 6.3: Average height of Bermuda grass grown in soils with increasing proportions (0, 25, 50 and 100%) of water-based drilling waste (WBM) at harvest. The Figure shown that no significant difference between the shoot high in the control and 25-W treatment and destructive effect of higher contamination level in treatment 50-W and 100-W respectively. Error bars represents the standard deviation from the mean value for triplicate samples

Root length and density are considered as important factor for phytoremediation of TPH and HMs (Wiltse et al., 1998; Suelee et al., 2017). Root length and density were different between treatments (Figure 6.4). The reduction in root length compared with the control treatment was 2.5, 22 and 93% in treatments 25-W, 50-W and 100-W respectively. The difference in root length between control and the 25-W treatment was not significant ($p > 0.1$).

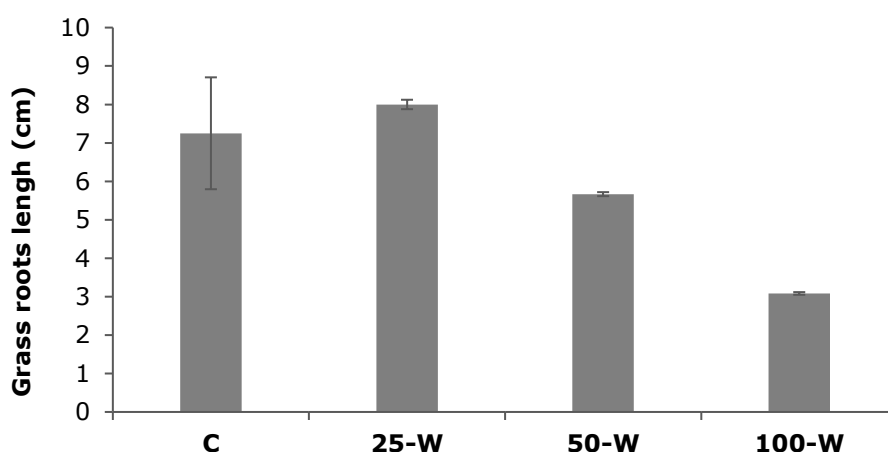


Figure 6.4: Reduction in average root length at harvest in Bermuda grass grown in soils with increasing proportions (0, 25, 50 and 100%) of water-based drilling waste (WBM). The Figure shown that no significant difference between the root high in the control and 25-W treatment and destructive effect of higher contamination level in

treatment 50-W and 100-W respectively. Error bars represents the standard deviation from the mean value for triplicate samples.

The result indicates significantly decrease in root length and density (p -value = 0.001) as contamination level increased. The results also show the root networks in the control and 25-W treatment are similar, distinctly larger, longer more fibrous and had a greater surface area than those in the 50-W and W-100 treatments (Figure 6.5). This would be expected to reflect positively on the ability of the grass to phytoremediation of hydrocarbons and HMs.



Figure 6.5: Reduction in roots density at harvest in Bermuda grass grown in soils with increasing proportions (0, 25, 50 and 100%) of water-based drilling waste (WBM).

Figure 6.6 shows the significant decline in leaf area with increase in contamination with petroleum hydrocarbons (p -value < 0.001).

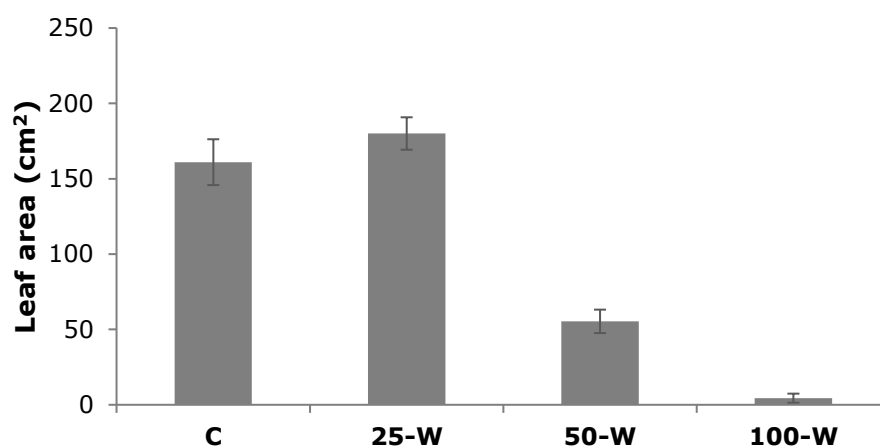


Figure 6.6: Effect of contamination on leaf area of Bermuda grass grown in soils with increasing proportions (0, 25, 50 and 100%) of water-based drilling waste (WBM). The

Figure shows destructive effect of TPH on reduction of the leaf area at harvesting after 60 days glasshouse experiment. The results confirm the negative effect of TPH high levels on the leaf area which may use as evidence to confirm the impact of high TPH conc. on the photosynthesis process in Bermuda grass plant. No significant effect observed at low TPH contamination level in control and 25-W treatments. The reduction in leaf area increases as the contamination by TPH increases. Error bars represents the standard deviation from the mean value for triplicate samples

All measures of plant growth (biomass, shoot weight and height, leaf area, and roots length and density) indicate the tolerance of Bermuda grass to grow in drilling waste is limited, with the grass only able to tolerate TPH concentrations below 7350 mg kg⁻¹. Greater concentrations of TPH appear to inhibit development of the root system and therefore growth. The Inhibition effects may result from that petroleum hydrocarbons retired Bermuda grass seed germination through direct and/or indirect effects. Direct effects raised due to the toxicity of petroleum hydrocarbons and its capability to break through the plant cell surface and solubilize the lipids of the cell membranes, causing tissue desiccation and death as suggested by Vaughn and Holser, (2007). Indirect effects resulted from the hydrophobic properties of petroleum hydrocarbons and its ability to coat the seeds restricting H₂O and O₂ uptake and/or through reducing the oxygen concentration in the root zone which causes reduction in root elongation and density, proliferation, viability, respiratory capacity, carbohydrate accumulation, hormone synthesis, and nutrient uptake as reported by Schnoor, 1997; Huang and Scott, 1999; White et al., 2003; Merkl et al., 2005).

This finding broadly supports the work of other studies in this area on the survival of different grass species in soils contaminated by petroleum hydrocarbons. For example, White et al., (2003) compare the growth and tolerance of Bermuda grass with different grass species in petroleum hydrocarbons contaminated soil, he reported that Alfalfa, crabgrass, fescue, and ryegrass all exhibited higher germination rates than bermudagrass in the crude oil-contaminated soil (8.0 wt. % TPH), and that Bermuda grass shows reduction in aerial plant parts biomass when exposed to high levels of contamination by petroleum hydrocarbons. Razmjoo et al., (2012), and Saraeian et al.,

(2016) reported reductions in shoot and root growth of Bermuda grass planted in soil containing 6 wt. % of petroleum hydrocarbons contaminants. Etemadi et al. (2015) observed reduction in chlorophyll content, water content and density resulted from planting Bermuda grass in soil contains 2.1 wt. % TPH, also he reported that the biomass measurements decreased as the soil pollutant content by TPH was increased.

6.3.4 Influence of Soil Properties

During irrigation, it was observed that treatments 100-W, 25-O, 50-O and 100-O resisted the infiltration of irrigation water and instead ponded water on the surface of the pot. As these are sandy soils this is undoubtedly attributable to the TPH content and the hydrophobic nature of these compounds which will repel water intrusion and result in a dry subsurface layer of soil (Edama et al., 2011). In turn this will affect the bioavailability of nutrients which govern plant growth in those treatments. In contrast water penetration in the other treatments (control, 25-W and 50-W) was good and reasonable grass growth was observed.

6.3.5 Survive of Bermuda grass in soils contaminated by HMs and up-take of trace elements

In general, the glasshouse experiment revealed that Bermuda grass could thrive on soils contaminated by low-medium concentrations of HMs and petroleum hydrocarbons without any visible adverse symptoms, although the heavy metal pollution can result in adverse effects on soil biological and biochemical properties such as plant growth, soil microbial diversity and activity, and genetic structure as reported by Singh et al., (2011) and Xie et al., (2016).

Table 6.3: Heavy metals concentration in the raw soil and shoot and calculation of translocation factor. The shown data is average of triplicate samples

Element	Concentration raw soil (mg kg ⁻¹)			Concentration in shoots Dry weight (mg kg ⁻¹)			Transfer factor (TF)		
	C	25W	50W	Control	25 -W	50-W	control	25 W	50W
Fe	5010	5209	5409	0.0	0.0	125	0.0	0.00	0.02
Cr	10.8	15.2	19.6	0.0	0.0	0.0	0.0	0.00	0.00
Mn	80.1	70.9	61.7	62.7	67.9	75.7	0.8	0.96	1.23
Cu	16.4	14.6	12.9	27.4	23.3	21.7	1.7	1.60	1.68
Zn	19.3	27.2	35.1	69.0	49.0	43.4	3.6	1.80	1.24
As	1.37	1.5	1.7	0.40	0.70	0.8	0.3	0.48	0.49
Cd	0.04	0.1	0.2	0.10	0.10	0.1	2.0	0.74	0.38
Ba	242	448	654	105	40.0	37.9	0.4	0.09	0.06
Pb	7.07	7.90	8.70	0.0	0.0	0.2	0.0	0.00	0.02
Co	1.47	1.50	1.60	0.3	0.7	0.8	0.2	0.48	0.52
Ni	5.25	6.00	6.80	1.1	1.6	1.7	0.2	0.26	0.25

Element concentrations in Bermuda grass shoots were measured at harvest, and a transfer factor (TF) calculated and illustrated in table 6.4. A TF > 1 indicates that the plant has accumulated metals, a TF =1 indicates a rather indifferent behaviour of the plant towards metal uptake, and a TF < 1 suggests that the plant excludes metals from uptake (Mingorance et al., 2007; Kandziora et al., 2017).

The data in Table 6.3 shown that Bermuda grass exhibited wide variation in the affinity to extract and accumulation of HMs such as Cr, Mn, Cu, Zn, As, Cd, Pd, Co and Ni in the plant areal part ((leaves + stems). Highest total accumulation was recorded in control sample for the metals (Zn, Cd and Cu respectively), then in treatment 25-W for the metals (Zn, Cu, and Mn respectively), then in 50-W treatment for (Cu, Zn and Mn respectively) in the descending order. The difference in ability to translocate the HMs from the soil to the plant shoots may attributed to the difference in physical and chemical characteristic between uncontaminated native soil and the soil samples contaminated by drilling waste.

The results also indicate the ability of Bermuda grass to extract and accumulate HMs such as Pb, Cd, As, Ni and Co is low (TF<1) in treatments 25-W and 50-W contaminated

by drilling waste. This suggested that plant not able to translocate the heavy metal into the shoot, especially for highly poisonous HMs such as Pd, Cd and As which indicates that Bermuda grass prefers to accumulate heavy metal in the soil and the root zone more than the plant shoots.

The results indicated that the capacity of soil to immobilize the HMs to be affected by the physical and chemical characteristics of the soil, increases with increasing the soil salts content (EC), and by the increases of organic carbon content at the rhizosphere zone which is consistent with the literature (Rieuwerts et al.,1998; Birge et al., 2000), and also affected by the differences in soil texture as reported by Mirzaei et al.,(2013) and Farrag et al.,(2011) , and also by the existence of clay minerals such as calcite in the contaminated soils as previously concluded by García-Sánchez et al., (1999) and Davis et al., (1987).

In general, the data in Table 6.3 shows that the ability of transfer and accumulate metals in plant shoots decreased as the contamination level by HMs and TPH increases in contaminated soil treatments. Both treatments 25-W and 50-W recorded $TF > 1$ for Zn, Cu and Mn in 50-W treatment suggesting that Bermuda grass has high affinity to accumulate theses metals in the plant shoots. Cu, Mn and Zn are essential nutrients for plant and plays a different role in photosynthesis, metabolic regulation, chlorophyll formation and activation for many enzymes needed during plant growth as reported by White and Brown, (2010). The transfer factor values of all treatments for the most poison and toxic heavy metals such as (Cr, As, Cd, Pd, Co and Ni) varied between 0.002 and 0.75 always < 1 except for Cd in control sample.

These results reflect those of Chatterjee et al., (2010) who also found that Bermuda grass has a lower ability to transfer the most poison HMs (Cd, Pd and As) in plant shoots comparing with a set of wetland plants. This also accords with the earlier observations

by Maiti et al., (2016), which showed that Bermuda grass exhibited higher translocation factor ($TF > 1$) for transfer Mn, Zn and Cu from soil to the aerial plant parts, and lower translocation factor ($TF < 1$) for Ni, Co and Pb, indicating immobilization of these metals in root system. The results related to the lower ability of Bermuda grass to transfer Pb to the shoots are in line with Soleimani et al., (2009), and to his conclusion linked this result with soil background metal contents and soil characteristics and that Bermuda grass would behave differently in terms of HMs uptake in different environmental condition depending on the soil quality, type, quantity of soil organic compounds, and the original HMs concentration.

Table 6.4 compares the results obtained from the analysis of HMs content in the leachate of soils contaminated by drilling waste before and after planting by Bermuda grass. The results confirm that planting of contaminated soil provide efficient method for reduction of HMs concentration in the leachate of the contaminated soil preventing their migration to groundwater and reduce the bioavailability in the food chain.

Table. 6.4 Concentrations of HMs in leachate before and after planting by Bermuda grass compared with the criteria of inert waste acceptable for landfill, and water supply specification according to the regulation issued by UK Environmental protection agency. The presented data are average of triplicate samples.

Metal	Conc. of HMs in leachate before planting (mg kg ⁻¹)			Conc. of HMs in leachate after planting (mg kg ⁻¹)			Inert waste criteria (mg kg ⁻¹)	Water supply criteria (mg L ⁻¹)
	C	25-W	50-W	C	25-W	50-W		
Cr	0.009	0.006	0.006	0.003	0.003	0.003	0.50	0.05
Mn	0.004	0.021	0.147	0.010	0.003	0.003	NL	0.05
Co	0.018	0.027	0.051	0.028	0.018	0.015	NL	NL
Ni	0.078	0.140	0.176	0.051	0.054	0.039	0.40	0.02
Cu	0.081	0.151	0.340	0.065	0.068	0.073	2.00	2.0
Zn	0.016	0.029	0.048	0.095	0.075	0.067	4.00	NL
As	0.020	0.012	0.013	0.019	0.026	0.028	0.50	0.01
Cd	0.001	0.002	0.001	0.001	0.001	0.000	0.04	0.005
Pb	0.006	0.013	0.010	0.005	0.004	0.005	0.50	0.025

NL not listed.

In treatment 25-W the reduction in chromium was 45.2%, Mn 87.6 %, Co 32.9%, Ni 61.0%, Cu 54.7%, Cd 46.0% and Pb 66%. In treatment 50-W greater reductions were

recorded for Mn, Co, Ni, Cu and Cd where the reduction percent was 97.7, 71.2, 77.8, 78.6 and 58.8 % respectively. Lower reductions compared to the 25-W treatment were recorded for Cr and Pb at 43.1 and 51.9 % respectively. Heavy metal analysis results from the leachate of unplanted contaminated soil and planted soil indicate that leaching of toxic compounds was not an important pathway for heavy metal to water supply, all toxic poison HMs (except As and Ni) are under the maximum allowed values in the water supply (Water Quality) Regulations in UK (Legislation.gov.uk, 2019). Also, the results indicated that the HMs concentration in the soil leachate after planting still within the guideline values to consider the treated drilling waste as inert waste according to the criteria proposed by UK environmental protection agency. (Appendix 1).

The results shown in Table 6.3 indicate the low transaction factor of toxic HMs to the plant areal part, and the results in Table 6.4 shows the reduction in values of HMs concentration in the leachate of planted treatments may use as proof of that Bermuda grass stabilizes the HMs and reduce their mobility and leachability and therefore ecological risk through Phytostabilisation mechanisms, where the HMs immobilized through absorption, accumulation, or precipitation within the soil and/or adsorption onto the roots.

The reduction in bioavailability of HMs results from planting of Bermuda grass in 25-W and 50-W treatments may be explained by the fact that the existence of petroleum hydrocarbons, the calcareous nature of drilling waste samples and the sandy loam texture of drilling waste treatments contributed through different mechanisms in immobilization of HMs. In similar studies, the HMs found adsorbed onto the calcite phase available in contaminated soil through adsorption mechanism as suggested by Park et al., (2010), or precipitated in the calcite mineral phase as suggested by Paulose et al., (2007) and De Benedetto et al., (2006). The HMs also may form complexes by bonding with surrounding organic and inorganic ligands such as chloride, carbonate and sulphate ions, which available in contaminated soil as suggested by Cataldo and

Wildung, (1978). The HMs also may immobilize in the root zone of the plant through incorporation into the fibrous root or into humus produced by the microorganism activities during the plant growth, or may be precipitated as insoluble forms and subsequently trapped in the soil matrix by the direct action of root exudates as reported by Oburger and Jones, (2018) and Tangahu et al., (2019).

This finding broadly supports the work of other studies in this area. Yoon et al., (2006) evaluate the phytoremediation potential of 36 plants including Bermuda grass and found that more than 95% of Pb, Cu and Zn metals accumulated in the soil, were less than 4% translocated to the areal part of the plant.

Over all, Bermuda grass shows reasonable ability to tolerate soil contaminated by drilling waste contains low HMs level, and immobilize the metals through Phytostabilisation (root stabilization) mechanism. The main drawbacks of HMs phytoremediation using Bermuda grass are related to the handling and disposal of the biomass obtained by harvesting the plant. Since, only essential heavy metals (Cu, Zinc and Mn) are accumulated in Bermudagrass areal part, and no toxic metals such as (Pb, Cd, As and Ni) transferred to the plant shoots, the grass biomass should be stored or disposed of appropriately, through confined in landfills or reused as compost for treatment of contaminated soil.

6.3.6 TPH Degradation

The biomass measurements illustrated in Section 6.3.2 and Figures (6.1, 6.2, 6.3, 6.4, 6.5 and 6.5) in this chapter showed that the shoot growth of Bermuda grass reduced scientifically (p-value <0.001) as the petroleum contamination levels in the soil increased. The same effect (p-value < 0.001) was recorded in roots density and leaf area as petroleum contamination levels increased up to 0.74 wt.% TOC (approx. 7350 mg kg⁻¹).

Despite the fact that hydrocarbon pollution depressed plant growth to some extent as the petroleum hydrocarbon concentration increase, the results indicate that the Bermuda grass can survive and tolerate petroleum hydrocarbons concentration below (0.74 wt. % approx. 7350 mg kg⁻¹ TOC), and it is can efficiently dissipate the petroleum hydrocarbon from amended drilling waste, indicating that phytoremediation, using this species is useful technique for remediation of soils contaminated by drilling waste polluted with petroleum hydrocarbons in level < 0.74 wt.% TOC. Similar results were obtained by Yateem et al., (2000) using alfalfa and perennial ryegrass as phytoremediater plant in soil contaminated by the presence of 1% TPHs.

The chemical analysis of the rhizosphere soil for treatments 25-W and 50-W demonstrated 99.0 and 98.0 % reduction in TPH content respectively (Table 6.6), compared with 32% reduction in the nonplanted controls after the bioremediation treatment for 60 days. The results indicate that the higher reduction in TPH content was in the rhizosphere region (almost 67 % in both treatments). The reduction of TPH in unplanted control may be attributed to the evaporation by the action of glasshouse temperature changes (25-35°C) during the glasshouse experiment period, or to the microorganism activity in this samples.

Table 6.5: TPH concentration in leachate of planted soil contaminated by drilling waste in treatments (25-W and 50-W) after glasshouse experiment for 60 days

TPH Fraction	TPH (mg kg ⁻¹) in leachate of planted treatments	
	25-W	50-W
n-C10	0	0
n-C11	0.00	0.00
n-C12	0.00	0.00
n-C13	0.00	0.00
n-C14	0.00	0.00
n-C15	0.00	0.00
n-C16	0.00	0.00
n-C17	0.66	1.32
n-C18	0.00	0.00
n-C19	0.00	0.00
n-C20	0.43	0.87
n-C21	0.69	1.37
n-C22	0.00	0.00
n-C23	1.40	2.81
n-C24	0.06	0.11
n-C25	0.00	0.00
n-C26	0.00	0.00
n-C27	0.00	0.00
n-C28	0.00	0.00
n-C29	0.00	0.00
n-C30	0.00	0.00
n-C31	0.00	0.00
n-C32	0.00	0.00
n-C33	0.00	0.00
n-C34	0.00	0.00
Total TPH conc.	3.24	6.48

The efficiency of Bermuda grass in removal of petroleum hydrocarbons from amended drilling waste samples was expected when compared to previous studies using Bermuda grass in remediation of petroleum hydrocarbons contaminated soil. In accordance with the present results, Kaimi et al., (2007) obtain similar results, by comparing the efficiency of Bermuda grass with another twelve-plant species in removal of TPH from soil contaminated by (1.5 wt.% TOC) and they found more than 65 % reduction in TPH caused by the plant and almost 37% reduction was lose by evaporation. The results also in line with Saraeian et al., (2016) who found that Bermuda grass reduce the

petroleum hydrocarbon content to approx. 40% from soil contaminated by 2 % wt. TOC, and with Razmjoo et al., (2012) where degradation was reported to be 41 % from soils contaminated by 6 % wt. TOC. This study also confirmed these findings and furthermore showed that Bermuda grass tolerate contamination by petroleum hydrocarbons levels below (0.74 wt. % TOC) and can maintain its growth when faced different stress applied in this experiment such as waste texture, calcareous nature of the waste, contamination by TPH and HMs and Desert climate changes.

The reduction of TPH content in planted soil usually attributed to biodegradative and non-biodegradative processes. In general, non-biodegradative processes include loose of petroleum hydrocarbons due to irrigation, evaporation, direct plant uptake and adsorption by soil. In this study, the leaching of petroleum hydrocarbons from contaminated soil was avoided by controlling the irrigation water below the water capacity of each treatment, and the loss by evaporation was measured and found less than the reduction by biodegradation. Direct plant uptake of TPH was assumed to be negligible because other studies have shown that heavy hydrocarbons such as fraction 2 (C10-C16), and fraction 3 (C16-C32) was not taken up by the plant, and its translocation from root to shoot is very limited due to their low solubility (O'Connor et al., 1992; Wild et al., 1992). In similar study, Binet and Leyval 2000 reported very low concentration of petroleum hydrocarbons adsorbed in roots tissue (<0.16 %) and (0.001%) in shoot tissue and 36 – 66% were dissipated resulted from planting ryegrass in soil contaminated by hydrocarbons, suggesting that the major part of petroleum hydrocarbon dissipation in rhizosphere soil was due to biodegradation or biotransformation mechanisms. In other study, Cofield et al., (2007) found negligible concentration from polyaromatic hydrocarbons in the plant biomass of fescue and switchgrass, and non-elevated concentrations from PAHs in the zucchini plant roots and shoots, and that PAHs were not detectable in the fruit when the contamination by PAHs was in the level 5% wt. TOC. Dadrasnia and Agamuthu, (2013) also observed that no

petroleum hydrocarbons remain in the plants in their study using different species of plants under different climates conditions.

Numerous researchers have established that the primary mechanism for the disappearance of both petroleum hydrocarbons and PAHs is rhizodegradation (EPA 2000b; Hutchinson 2003; Kaimiet al., 2007). In this mechanism, the TPH reduction in contaminated soil obtained mainly by the influence of plants and the microbes associated with them, the dissipation of TPH and PHAs mainly brought out by microorganisms which enhancing mineralization of oil in soil. Also, the production of root exudates stimulated microbes in soil to degrade hydrocarbons.

6.3.7 Microbial Interaction

To confirm the rhizodegradation mechanism, microbial diversity and activity in the planted and unplanted contaminated soil was assessed using Biolog plate GN2 for gram-negative bacteria as described in Section 2.4.2.3. in Chapter 2.

The measurements of the average metabolic response (AMR) in planted control (uncontaminated native soil), 25-W and 50-W treatments indicated that vegetation of contaminated soil by Bermuda grass enhanced the microbial activity in the rhizosphere zone in contaminated soils only and reduce it in control sample. Figure 6.7 compares the ARM and CMD for all treatments (irrigated and planted control, 25-W and 50-W treatments with unirrigated, unplanted control, 25-W and 50-W treatments). In the same figure it is clear that the efficiency of substrate mineralization by soil microorganisms is higher in irrigated and planted treatments. The same results obtained by comparing the AMR and CMD between unirrigated, unplanted soils with irrigated and planted treatments are shown in appendix 4). The results also shown increase in the carbon metabolic diversity (CMD) (despite the identical composition of

the microbial community) in planted contaminated soil and was much higher comparing with the control sample (Figure 6.8).

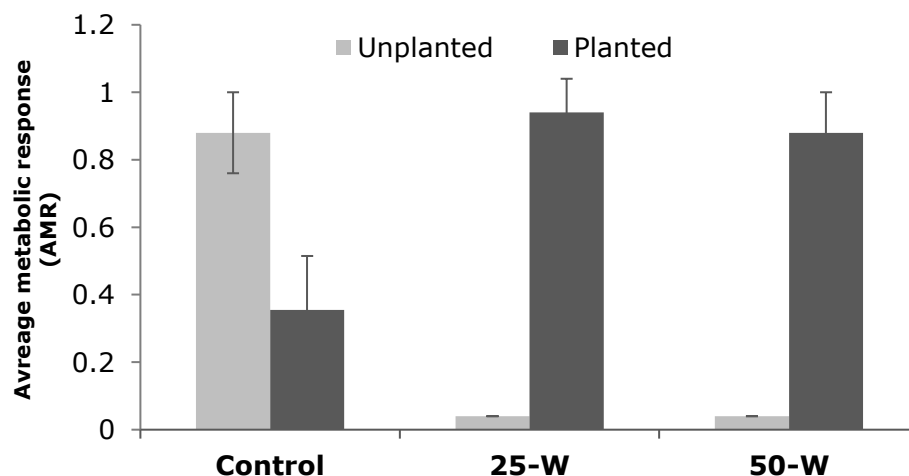


Figure 6.7. Average metabolic response in planted and unplanted treatments. The Figure shows the metabolic response by soil microorganisms as an indicator of microbial respiration in irrigated and planted control and contaminated soil 25-W and 50-W, and the efficiency of substrate mineralization by soil microorganisms is higher than unirrigated, unplanted control and 25-W and 50-W treatments. The error bar represents the standard deviation of the mean value for triplicate samples.

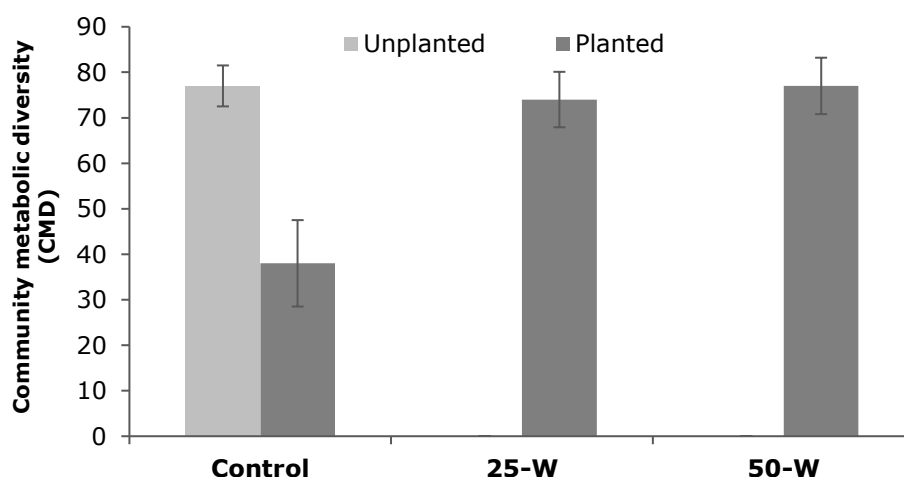


Figure 6.8. Microbial community metabolic diversity in planted and unplanted treatments. The Figure shows scientifically increase in treatments contain higher TPH concentration (25-W and 50-W contain (3650 and 7350 mg kg⁻¹ TOC respectively) comparing with control sample contain 150 mg kg⁻¹ TOC. Error bars represent standard deviation of the mean value of triplicates samples

The elevation in the microbial activity and diversity in the rhizosphere zone in treatments 25-W and 50-W as shown in Figure 6.7 and Figure 6.8 linked well with the high rate of dissipation of petroleum hydrocarbons in both treatments, and indicates

that the roots of Bermuda grass have important role in degradation of petroleum hydrocarbons, and that petroleum hydrocarbons in treatment 25-W and 50-W act as sources of carbon for microbial growth and activity and provided suitable environment to enhance the microorganism activities, which reflects on the dissipation of petroleum hydrocarbons in the contaminated soil .

The reduction of microbial activity and diversity in control samples may linked with lower carbon content in the control planted soil comparing with 25-W and 50-W treatments contaminated with high concentrations of petroleum hydrocarbon (150, 3675 and 7350 mg kg⁻¹ TOC respectively). Also, the reduction in activity and diversity may attribute to the different in soil physicochemical properties between control and contaminated treatments, and to the different initial microbial communities which expected to have different inherent microbial activity and diversity as reported by Bundy et al., (2002) and Alrumman et al., (2015).

The results, also indicated that the dissipation of petroleum hydrocarbon was take place under rhizoremediation (phytostimulation) mechanism, where the microorganisms population present in the rhizosphere or near the root zone in contaminated soil breaking down petroleum hydrocarbons via the use of their enzymes into nontoxic and harmless product and make it more bioavailable through the metabolic transformation processes as concluded in several studies that have assessed microbial counts in petroleum hydrocarbons contaminated soils. This is consistent with the findings of Maqbool et al., (2012), and (Gkorezis et al., 2016) who concluded that the addition of plants and soil amendments to contaminated soil, increases bacterial counts compared to unplanted soils and enhance the degradation of organic materials.

6.3.8 Soil enzymes activity assays

Dehydrogenases enzymes activity (DHA) represent the most important enzymes in rhizosphere soil. DHA belonging to the 'oxidoreductases' class and can be used as

biological indicator of overall microbial respiratory activity used by microorganisms in the soil to break down organic compounds. This enzyme occurs only within soil bacteria (e.g. genus *Pseudomonas*, with *Pseudomonas entomophila* as most abundant) as reported by Burns, (1982). The metabolic processes by DHA enzymes occur in abundance in healthy microorganisms (Bolton et al., 1985; Quilchano and Marañón, 2002; Salazar et al., 2011).

In order to assure the microorganisms activity in rhizosphere soil of the planted treatments, the soil dehydrogenase enzyme activity DHA was measured at the end of the pot experiment and used as indicator of soil quality changes resulting from phytoremediation using Bermuda grass. The results (Figure 6.9) shown an increase in DHA activity in treatments 25-W and 50-W after they were cultivated by Bermuda grass compared to little change over the same period in the control treatment (uncontaminated native soil).

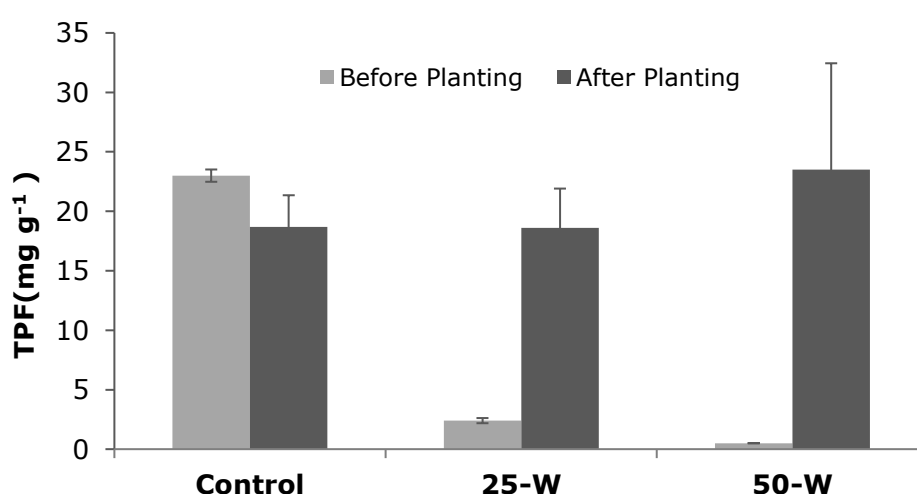


Figure 6.9: The activity of soil DHA in 150, 3675 and 7350 mg kg⁻¹ TOC contamination level. Dehydrogenase activities (reduction of TTC) from grass planted and unplanted soil treated before planting. unpolluted soil is not shown. Error bar represent the standard deviation about the mean of triplicate samples

Data for unvegetated the activity of DHA enzymes increased, together with an increase in the contamination level. The DHA activity data showed that the enzymatic

dehydrogenation effect of Bermuda grass on the organic matter was greatly enhanced under petroleum hydrocarbon contamination in the level below 7350 mg kg⁻¹ TOC.

The obtained results are positively correlated with the measurements of average metabolic response (AMR), and carbon metabolic diversity (CMD) in the planted treatments and the dissipation rate of TPH in planted soil. DHA in all the planted contaminated soils was significantly higher than that in the unplanted soils at the level (p-value < 0.01). This may be a consequence of the hydrocarbons stimulating the formation of DHA and suggests that accelerated microbiological degradation of petroleum hydrocarbon contaminants resulted as reported by Kaczyńska et al., (2015) and Alrumman et al., (2015).

The results obtained in the current study, confirmed that Bermuda grass has a significant positive effect on degradation of hydrocarbons through rhizodegradation mechanism, and stabilization of heavy metals from drilling waste through the rhizosphere effect, and it can adapt with the Libyan Desert climate, therefore it is recommended as a useful candidate for in-situ phytoremediation of drilling waste in Libya when the petroleum hydrocarbons concentration below 0.74 wt.% TOC.

6.4 Conclusions

This chapter aimed to evaluate Bermuda grass as a potential candidate for the phytoremediation of petroleum hydrocarbons and heavy metals in contaminated drilling waste in conditions similar to the Libyan Desert. Throughout this study, several evidences were presented that Bermuda grass is an important plant species that can be effectively applied as phytoremediator for stabilisation of heavy metals and degradation of petroleum hydrocarbon from drilling waste after amending of drilling waste by adding native soil as bulking agent. The major findings of this study include:

- Bermuda grass can efficiently survive and tolerate the Desert climatic condition, and relatively tolerant to soils contaminated by heavy metals and petroleum hydrocarbons
- Phytoremediation of heavy metals and petroleum hydrocarbons using Bermuda grass has proven to be a feasible method for remediation of drilling waste contains low concentration heavy metals, and petroleum hydrocarbons with concentrations less than 7350 mg kg⁻¹ TOC. The presence of higher TPH concentrations in the contaminated soil inhibited emergence of Bermuda grass
- The use of Bermuda grass enhances the microbial enumeration, diversity and DHA enzyme activity in the root zone which resulted in dissipation of petroleum hydrocarbon through Rhizodegradation mechanism and stabilisation of the HMs and reduce their mobility and leachability through Phytostabilisation mechanisms, where the HMs immobilized through absorption, accumulation, or precipitation within the rhizosphere soil and/or adsorption onto the roots
- Amendment of drilling waste by addition of native soil have larger particle size increase the soil porosity, aeration, oxygen diffusion and water holding capacity in

contaminated soil, thus change the waste physical properties and enhance the microbial activity and reflects positively on the phytoremediation efficiency of Bermuda grass

The present investigation clearly demonstrates that Bermuda grass has the potential to tolerate a Libyan Desert climate, low levels of HMs and relative tolerance for petroleum hydrocarbons below 7350 mg kg⁻¹ TOC. This indicates the potential of this plant species for decontamination of drilling waste contained by low-medium levels of HMS and TPHs (under glasshouse conditions). The performance of Bermuda grass is of major relevance for the improvement of in-situ phytoremediation technology for the treatment of contaminated soil generated from the gas and oil industry in Libya, providing low cost and ecologically friendly technologies for in-situ treatments of contaminated soil.

This study provides basic information for applying phytoremediation as a waste management option in Libya, and background information to expand the current understanding for the use of native plants for in-situ treatment of soils contaminated by HMs and TPHs. The obtained findings suggest that there are multiple challenges that need to encounter until phytoremediation will become an established technology in Libya. Future research should focus on studying the impact of real Desert weather changes, irrigation control, reuse or disposal of grass biomass produced during the phytoremediation of drilling waste. A better understanding of many aspects of the basic science needs to develop to apply efficient phytoremediation systems for the treatment of contaminated soil.

Chapter 7: Conclusions and future work

Protection of the environment from pollutants associated with waste generated during drilling of wells for exploration or production of gas and oil is a major concern especially in developing countries such as Libya. Therefore, it is very important to reduce the release of petroleum hydrocarbons and heavy metals into the environment.

In Libya traditional waste management solutions for drilling waste are difficult to implement. The main problems are lack of appropriate infrastructure and technical experience needed for management and disposal of this type of waste.

Typically drilling waste has been temporarily stored in earthen pits close to drilling operations before disposal to land or permanent burial in the pits. This management option provides a simple and low-cost approach but is unsuitable for wastes containing high concentrations of oil, salt, toxic metals or other harmful components that could migrate and contaminate ground water resources or the surrounding environment.

As drilling operations increase accumulation of waste is becoming a more pressing issue for the country and a simple, sustainable and effective solution to the waste problem is highly desirable. Solidification/Stabilisation and phytoremediation approaches represent sustainable waste management options and are particularly suitable for situations where infrastructure and resources limit the feasibility of conventional remediation strategies.

This thesis sought to determine the toxicity of drilling waste generated during oil and gas drilling operations in Libya, and to assess and investigate the effectiveness of sustainable *in-situ* waste management options. Solidification/Stabilisation and phytoremediation were selected and tested to see if they might prove to be suitable waste management options for Libya.

In order to achieve this objective, the S/S of drilling waste through geopolymerisation was tested utilizing industrial by-products and kaolin clay as a binder. Phytoremediation of soil contaminated with drilling waste was also investigated using a Bermuda grass, warm season grass and a drought tolerant species known to accumulate trace elements and grow in hydrocarbon contaminated soils.

Where appropriate the leaching characteristics of the treated drilling waste were compared to the UK acceptance criteria for waste at landfill to classify the waste as inert or hazardous (BS EN 12457-2 appendix 1). The durability and strength of S/S systems was compared using the USEPA criteria for inert waste landfill (USEPA, (2000), and to the British criteria for reuse/ recycle the solidified waste in the production of precast concrete masonry units (BS 6073-1:1981).

In Chapter 3, the focus was on developing a suitable geopolymer recipe that used actual samples of drilling waste collected during drilling operation in Libya, and locally available materials as a binder and additives. Lab-scale experiments assessed the effectiveness of using both steel industry (SI) and brick industry remains (BR) as starting materials but the materials formed with very poor structure resulting from poor geopolymer gel production. The failure to form the geopolymer gel in sufficient quantity to produce a solid matrix that was resistant to leaching and had a high strength was attributed to a high $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio and the use of a high concentration of alkali activator. Both factors lead to a process known as alkali-silica reaction (ASR) that results in poor binding capacity and the formation of loose and incoherent systems that cannot meet the leachability and strength requirements acceptable for safe landfill. Efflorescence formation caused by the presence of unreacted alkali activator and/or the migration of dissolved salts within a porous material to its surface was observed in the materials produced. Petroleum hydrocarbon content was also observed to be an important factor with higher TPH concentrations significantly affecting the properties of the materials produced.

It was therefore clear that successful S/S of this waste would be most likely achieved through the using of aluminosilicate materials with higher Al_2O_3 content to optimise the $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio needed to form geopolymer gel, and reduction of the alkali activation concentration to the level where it can play its role in the formation of geopolymer gel with better microstructure and not lead to the formation of efflorescence alongside a reduction in TPH concentration.

Based on these findings and consideration of the main factors affecting geopolymer performance, the ability of natural kaolin, that contains high amounts of Al_2O_3 , to produce geopolymers with drilling waste was assessed in Chapter 4. Natural kaolin clay with a $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of 2, and metakaolin clay (produced by the ignition of kaolin clay) with a $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of ~ 1.8 was tested in geopolymer-waste systems. Performance of the materials generated was assessed by determining the degree of geopolymerisation reaction, density, water absorption, total void volume, leachability of salts, HMs and petroleum hydrocarbons, and analysis by FTIR and XRD.

The work highlighted the importance of the addition of lime to enhance the transformation of raw materials (kaolin and drilling waste) into a solid matrix and strengthen the geopolymers produced by encouraging the formation of CSAH and CSA gels. Further, the addition of lime was found to significantly reduce efflorescence, increase pH and decreases cation exchange capacity and therefore mobility of HMs and leachability of TPH from geopolymer-waste systems. At TPH concentrations above 3.4 wt. % TOC, alkali activator concentrations >8 M and at high water: solid ratios a destructive effect on microstructure and cohesiveness properties of kaolin-waste S/S systems was observed resulting in materials with poor strength, greater leachability and efflorescence issues.

Overall natural kaolin was demonstrated to be a suitable starting material for transformation of drilling waste to a monolithic solid system through geopolymerisation.

With careful selection of materials and optimisation of the starting mixtures the physical and chemical properties of some of the kaolin-waste solid matrices produced met the regulatory criteria for safe landfill (appendix 1).

The work confirmed the suggestion of other researchers that the optimum geopolymer formula to achieve materials of the highest performance requires (3.0-3.8) $\text{SiO}_2/\text{Al}_2\text{O}_3$, (1-1.6) $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and (10-12) $\text{H}_2\text{O}/\text{Na}_2\text{O}$. The maximum degree of geopolymerisation, optimum microstructural properties and least leachability was achieved using kaolin-waste geopolymer recipes with a formula of (3.2-3.4) $\text{SiO}_2/\text{Al}_2\text{O}_3$, (1-1.3) $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and (8.4-13) $\text{H}_2\text{O}/\text{Na}_2\text{O}$.

The FTIR and XRD results indicated that kaolin clay produced geopolymers with better physical and chemical performance than those produced using metakaolin. Kaolin-waste geopolymers showed a higher degree of geopolymerisation and formation of new phases including Hydrosodalite, katoite and hydrotalcites which confirmed the transformation of kaolin-waste mixtures in to geopolymers with a denser lattice, higher stability and higher specific surface area allowing for higher sorption and adsorption capacity.

The results of microstructure studies show formation of kaolin/zeolite based geopolymers contains Hydrosodalite phase, and calcium-based geopolymer contains katoite phase which take advantage of all these constituents: high surface area, pore volume and adsorption capacity from zeolites (Hydrosodalite), and Katoite and strength and support from geopolymer matrix as reported Rožek and Mozgawa, (2019). Hydrotalcites phase also have unique characteristics such as cation-exchange ability, anion-exchange ability, surface adsorption capacity as reported by many researches (Shekoohi et al., 2017)., this explains the results obtained from leachability tests and confirm the production of a good quality S/S matrix able to immobilize the HMs and

encapsulated the petroleum hydrocarbon and transform the hazardous drilling waste to inert or non-hazardous waste.

These findings help to understand the mechanisms of transformation of kaolin and drilling waste materials through geopolymerisation and/ or alkali activation and suggests that these kaolin-based materials, cured in conditions relevant to the Libyan Desert environment, demonstrate the suitability of investigating geopolymer approaches for the practical management of drilling waste for the oil and gas industry in Libya.

Improvement of the properties of these kaolin-based S/S systems was investigated by examining the effects of addition of Na_2SiO_3 and use of a finer kaolin particle size (Chapter 5). The study also included an investigation of the durability of kaolin-waste systems by exposure in the Libyan Desert for more than a year to establish the effect of weather changes on strength and leachability. In this study, also, kaolin-waste (S/S) geopolymers compared with similar systems produced using Portland cement. The addition of Na_2SiO_3 , slow down the alkali activation reaction, reduce the formation of gel and accelerated the setting time. It also behaved as a healing agent and fillers for S/S system have poor microstructure properties (contain 3.4 wt. % TOC), which reflected in enhancement of durability of these systems by the reduce the HMS and TPH leachability and improve strength characteristics of solidified kaolin-waste systems to which it was added.

No evidence was found to support the use of a finer kaolin binder particle size to enhance reactivity in kaolin-waste systems containing TPH concentrations < 0.6 wt. % TOC, but an improvement was observed where TPH concentrations were greater (3.4 wt. % TOC). The effect of particle size may be attributed to the greater surface area provides enhancing the reactions and encouraging formation of more geopolymer gel during the early reaction stages.

Exposure of samples to the Libyan Desert climate confirmed the efficiency of both S/S system, PC-waste and the kaolin-waste geopolymers in convert the hazardous drilling waste into inert or nonreactive hazardous waste acceptable for selected environmental engineering applications such as safe land disposal or construction applications require low mechanical strength such as producing blocks, fixing bricks or to be used in sublevel construction of roadways in the place of generation which offering a sustainable, cost-effective approach that brings environmental and economic benefits.

After 1 year in the Libyan desert solidified geopolymer-waste and PC-waste systems did not appear to be substantially affected. Physical and chemical properties remained relatively unaffected except for a slight decline of in mechanical strength in the kaolin-waste geopolymers containing 3.4 wt. % TOC over the first 90 days. Despite this reduction the material still had sufficient mechanical strength for safe burial.

Based on measurements of compressive strength on the geopolymer-waste systems, these materials are also likely to find suitable environmental applications in the gas or oil drilling sites in the Libyan Desert. Drilling waste containing TPH concentration approaching 3.4 wt. % TOC could be transformed into solid material using kaolin as binder and the final solidified matrix safely disposed of in properly selected burial sites close to the drilling operations sites. Alternatively, solidification using a fine particle size kaolin binder and Na_2SiO_3 to improve the strength, would allow the material to be used in pedestrian paving or similar applications. Solidified matrixes produced using kaolin-waste system where TPH content are lower (0.59 wt. % TOC) could be safely buried or used in ground improvement works at drilling site or recycled for the production of construction materials such as blocks and bricks where higher compressive strengths are required.

An alternative to geopolymerisation for sites where oil industry waste has been disposed of to the land surface is phytoremediation. Bermuda grass (*Cynodon dactylon*), a

species known to be drought tolerant and to survive in such harsh environments was tested to see if it had sufficient potential to be used in this way.

Grass growth and physiology in non-contaminated and contaminated drilling waste was evaluated. Plant biomass (roots and shoots) was affected by increasing concentrations of TPH. Roots appeared more affected than shoots and germination was hindered in treatments contain more than 7350 mg kg⁻¹ TOC. Bermuda grass was however shown to tolerance to survival in soil contaminated by petroleum hydrocarbons in a level below (0.74 wt.% TOC approx. 7350 mg kg⁻¹). Higher petroleum hydrocarbon concentration did significantly affect plant growth in terms of reducing plant biomass and growth rate. Nevertheless, the enhancement of microbial activity and diversity in the rhizosphere encouraged the potential of this plant species to be successfully used in the remediation of soils contaminated by low-medium concentrations of petroleum hydrocarbons.

Bermuda grass could not be considered as an active heavy metal removal species as it was not able to uptake significant amounts of heavy metals and accumulate selected trace elements in its shoots. The results shown lower transaction factor of toxic HMs such as (As, Ni, Co, Cd and Pb) from the soil to the plant areal parts, and reduction in values of HMs concentration in the leachate of planted treatments which indicate that Bermuda grass stabilizes the HMs in the rhizosphere soil zone and reduce their mobility and leachability through Phytostabilisation mechanisms, where the HMs immobilized through absorption, accumulation, or precipitation within the soil and/or adsorption onto the rhizosphere soil.

From the study, it was clear that phytoremediation using Bermuda grass could be applied for soil contaminated by drilling waste, but higher TPH concentration (> 0.74 wt% TOC 7350 mg kg⁻¹) inhibit using this approach. More studies using warm and cold session species need for comparison purpose

Limitation and recommendations for future work

Although the findings of this thesis open a good viewpoint for the efficiency of both selected approaches. The research results can be used as ground information for further studies, more advanced and specified research in the context of treatment of drilling waste generated from the oil and gas industry in Libya is needed, in both approaches (S/S) or phytoremediation. The additional studies would further complement and validate this work.

In the geopolymerisation of drilling waste approach, further work is necessary to study the effect of other factors can improve the physical and strength properties of Kaolin-waste (S/S) systems. For example:

- Studying the effect of increasing binder contents to 30-40 %, and using kaolin binder with finer particle size (< 100 micron) in enhancement of formation of more gel and its impact on the leachability and durability properties of S/S geopolymer based systems.
- Studying the impact of using lower water: solid ratios between (0.2-0.25) and /or addition of plasticizers in improvement of the microstructure properties, and enhancing the durability of S/S geopolymer based system to qualify the solidified kaolin-waste geopolymers to reused in environmental applications require higher mechanical strength
- Studying the effect of addition of adsorbent materials such as (Natural diatoms, activated carbon) or fillers such as (steel industry by-products rich in MgO) available in Libya in improvement of both microstructure and strength properties of kaolin based geopolymers.

Using a phytoremediation approach, the results obtained in this thesis can be used as baseline information for scale-up phytoremediation of contaminated sites using different plant species. Substantial further work is required to properly assess the potential for phytoremediation of soils contaminated by drilling waste and expand the findings reported in this thesis. The most important future studies have been identified and discussed in the following:

- Conducting field experiments in the place of generation of drilling waste to assess the response and effectiveness of Bermuda grass in the remediation of contaminated soils under real condition to highlight the differences between growth in the glasshouse and the real Libyan Desert climate. Several researches were found that the grasses planted in field had root system better than those planted in pots in glass house condition, as root growth was not confined to a small volume such as occurs within the pots. In addition, plants in the field can regenerate from underground rhizomes, which enhance the grass growth and the biomass and enhance the microbial activity and diversity in the rhizosphere zone.
- Although the Libyan Desert climate were simulated as much as possible in this study the controlled condition of glasshouse did not allow Bermuda grass to experience the unpredictable environment changes in Libyan desert climate. A long-term investigation should be conducted to study the effect of Libyan desert weather changes such cold weather during the winter session, wind, change in humidity on the biomass, physiology properties, microbial activity and diversity, and phytoremediation performance of Bermuda grass under the stress of real desert condition
- Future studies still needed to indicate more precisely the phytoremediation mechanisms used by Bermuda grass. Analysing metal and hydrocarbons speciation in plant tissue (Roots and shoots), in addition to metal and hydrocarbons speciation in soils in intervals for long period, and after harvesting the above-ground part of the plant

many times can provide a better understanding of the phytoremediation mechanisms used by Bermuda grass to stabilize the HMs and dissipation of petroleum hydrocarbons

- The current work focused solely to assess Bermuda grass as warm season tolerant grass, and as a potential candidate to remediate soils contaminated by HMs and TPH. Future work still needed to examine the feasibility of using another native grass species, warm-season grass such as Switchgrass (*Panicum virgatum*), and cold season grass such as Tall fescue grass (*Festuca arundinacea*) or Perennial ryegrass (*Lolium perenne*), or combination from both species in phytoremediation of soils contaminated by drilling waste and comparing the efficiency of selected species with Bermuda grass
- The results obtained in this work indicate that planting of Bermuda grass in polluted soil induces the microbial and enzyme activities that resulted in the dissipation of petroleum hydrocarbons. More research needed to indicate how to improve the plant growth and enhancing the Rhizodegradation of petroleum hydrocarbons. Future studies still needed to examine the effect of different agricultural work techniques on the improvement of plant growth in contaminated soil. Similar studies indicate reasonable enhancement in plant growth by applying a multi-process system, including land farming (aeration and light exposure) (Azubuike et al., 2016), adding of composite and bulking agent (Rhykerd et al., 1999), microbial inoculation (introduction of contaminant degrading bacteria) (Karimi et al., 2018) to facilitate the aerobic conditions in the rhizosphere and improvement of the microbial growth and diversity to enhance and accelerate the degradation of TPH in drilling waste or contaminated soil contain higher TPH concentration.
- Although Bermuda grass has been relatively efficient for the remediation of contaminated soil sites, due to the limited time, no data available in this thesis on the use or disposal of harvested biomass from phytoremediation sites. More studies needed to answer the following questions: -

- Is it possible to utilize the obtained biomass as feed for animals?
- Is it possible to reuse the obtained biomass as composting material and bulking materials for phytoremediation of other contaminated sites?
- Is there any apprehension regarding the fate of accumulated pollutants in harvested plants and the chance to enter it into the food chain?
- Is there any chance of occupational exposure to those who have direct contact with biomass processing, utilization, and/or disposal?

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Appendixes

**Appendix 1. Criteria for granular waste acceptable at landfills
(Transposed from Council Decision annex 2003/33/EC)**

	Inert Waste Landfill	Stable nonreactive hazardous waste & nonhazardous waste co-disposed with (SNRHW)	Hazardous waste landfill
TOC w/w %	3	5	* 6
L.O.I w/w %			10
BTEX (mg/kg)	6		
PCBs (7 congeners) (mg/kg)	1		
Mineral oil C10-C40 (mg/kg)	500		
PAHs (mg/kg)	100		
pH		>6	
Limit values (mg/kg) for compliance leaching test using BS EN 12457 at L/S 10 l/kg			
As (arsenic)	0.5	2	25
Ba (barium)	20	100	300
Cd (cadmium)	0.04	1	5
Cr (chromium (total))	0.5	10	70
Cu (copper)	2	50	100
Hg (mercury)	0.01	0.2	2
Mo (molybdenum)	0.5	10	30
Ni (nickel)	0.4	10	40
Pb (lead)	0.5	10	50
Sb (antimony)	0.06	0.7	5
Se (selenium)	0.1	0.5	7
Zn (zinc)	4	50	200
Cl (chloride)	800	15000	50000
F (fluoride)	10	150	500
SO4 (sulphate)	#1000	20000	50000
Total dissolved solids (TDS)	4000	60000	100000
Dissolved organic carbon at own pH or pH7.5-8.0@	⊕500	800	1000

* Either TOC or LOI must be used for hazardous wastes

If an inert waste does not meet the SO₄ L/S10 limit, alternative limit values of 1500 mg/l SO₄ at C0 (initial eluate from the percolation test (prCEN/TS 14405:2003)) AND 6000 mg/kg SO₄ at L/S10 (either from the percolation test or batch test BS EN 12457), can be used to demonstrate compliance with the acceptance criteria for inert wastes.

+ The values for TDS can be used instead of the values for Cl and SO₄.

@ DOC at pH 7.5-8.0 and L/S10 can be determined on eluate derived from a modified version of the pH dependence test, prCEN/TS 14429:2003, if the limit value at own pH (BS EN 12457 eluate) is not met.

⊕ In the case of soils, a higher TOC limit value may be permitted by the Environment Agency at an inert waste landfill, provided the DOC value of 500mg/kg is achieved at L/S 10 l/kg, either at the soil's own pH or at a pH value between 7.5 and 8.0.

Appendix 2. XRD Analysis for raw materials, K-waste, MK-waste and PC-waste (S/S) systems

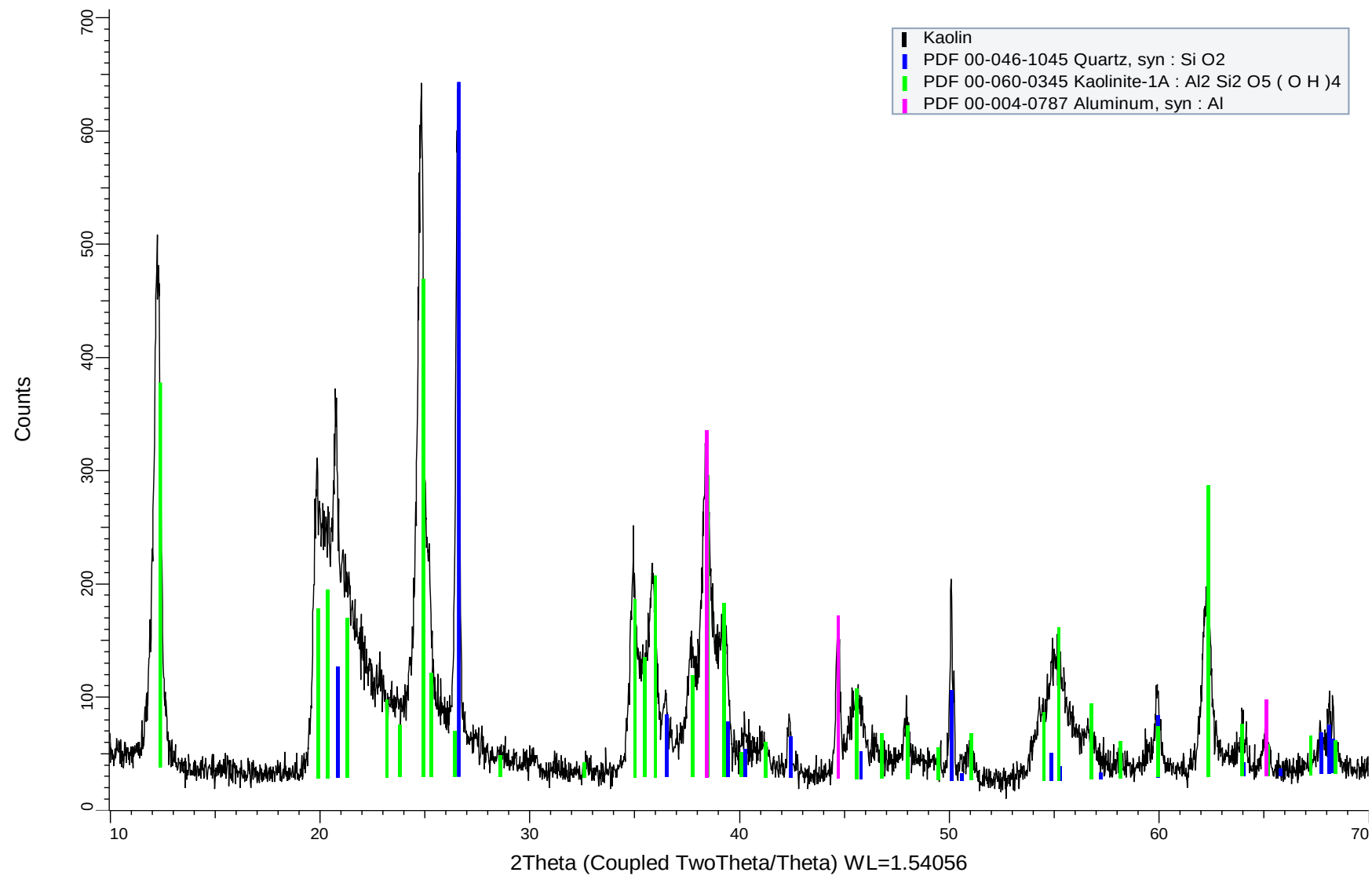
Measurements were carried out on a Hiltonbrooks PW1050 x-ray diffractometer using CuK α radiation (wavelength 0.15406 nm).

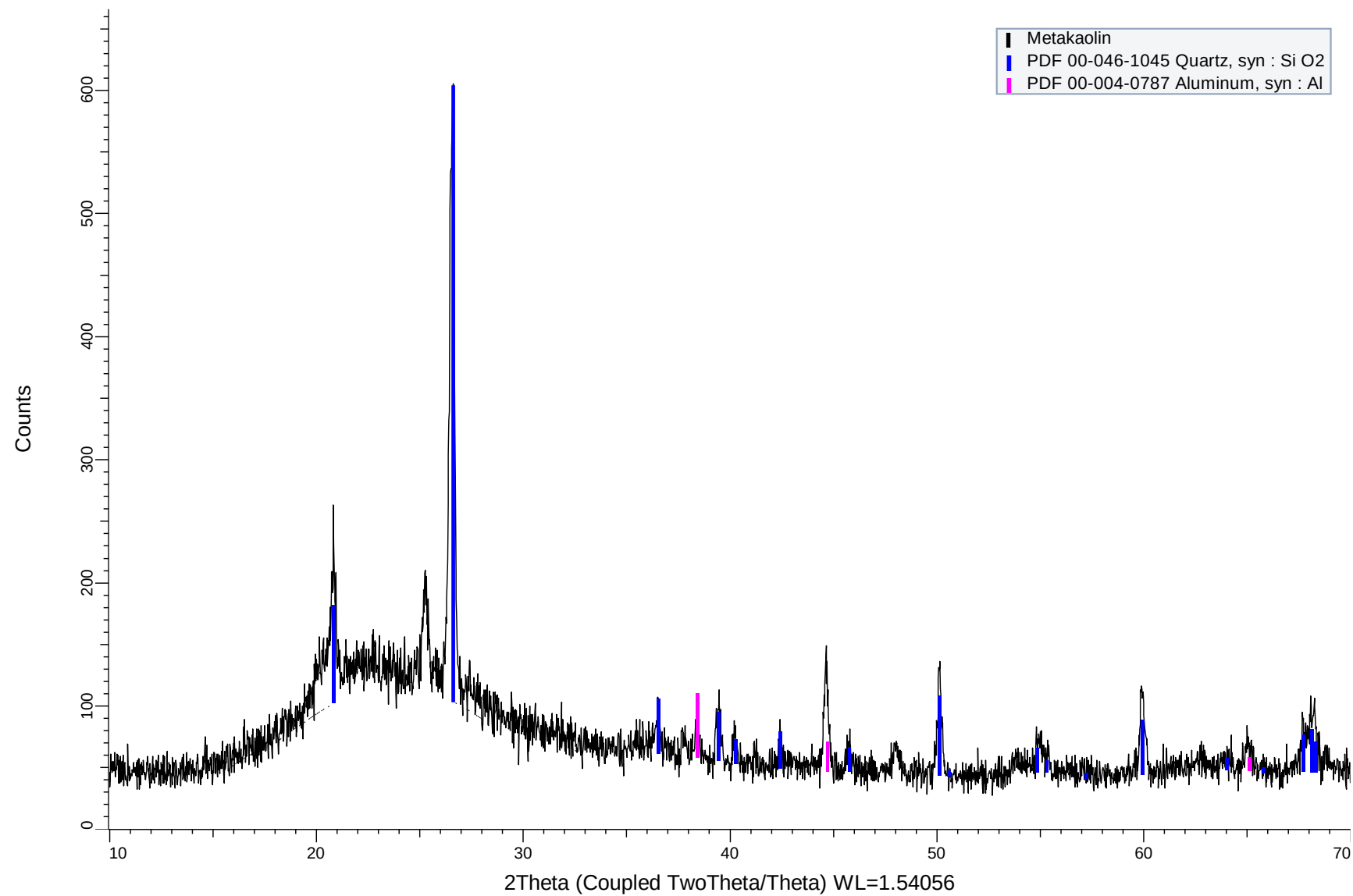
Data processing and phase identification was done using Bruker DIFFRAC.EVA software and the ICDD PDF-2 2015 database.

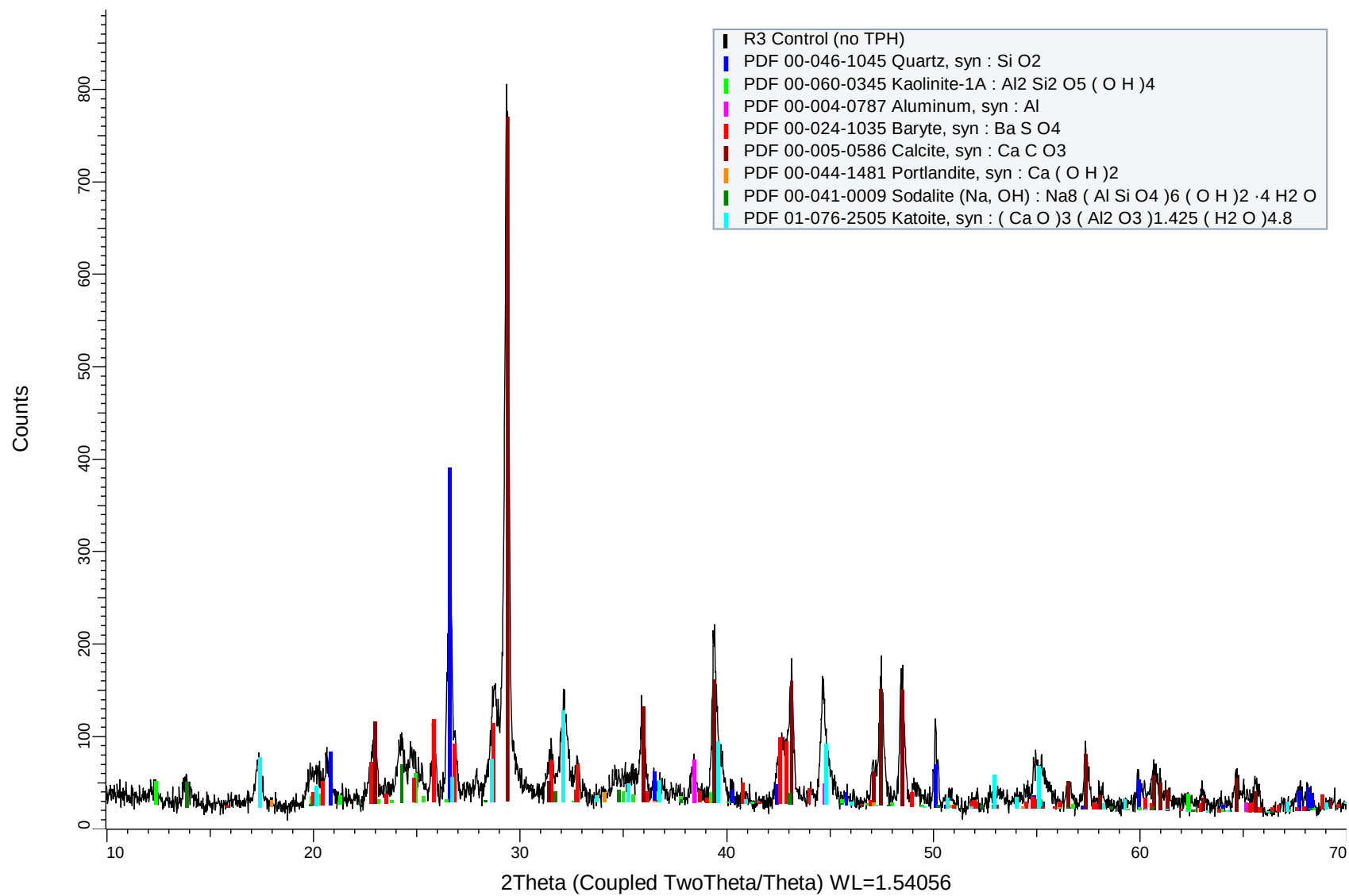
All the diffraction patterns include peaks for metallic aluminium, which is attributed to the sample holder.

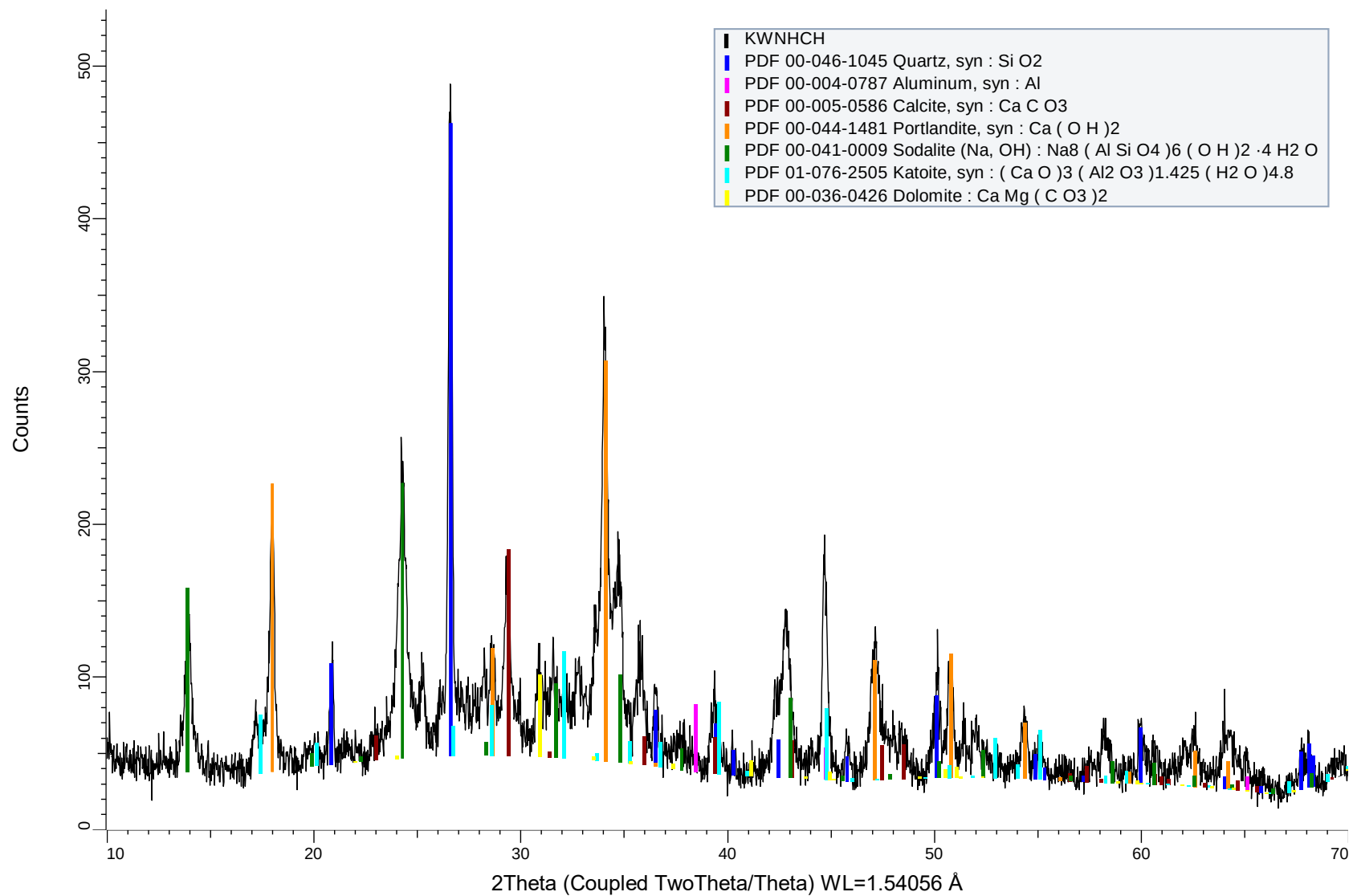
Some of the diffraction patterns include very broad peaks, which have been modelled as part of the background (e.g. metakaolin); these are attributed to amorphous components.

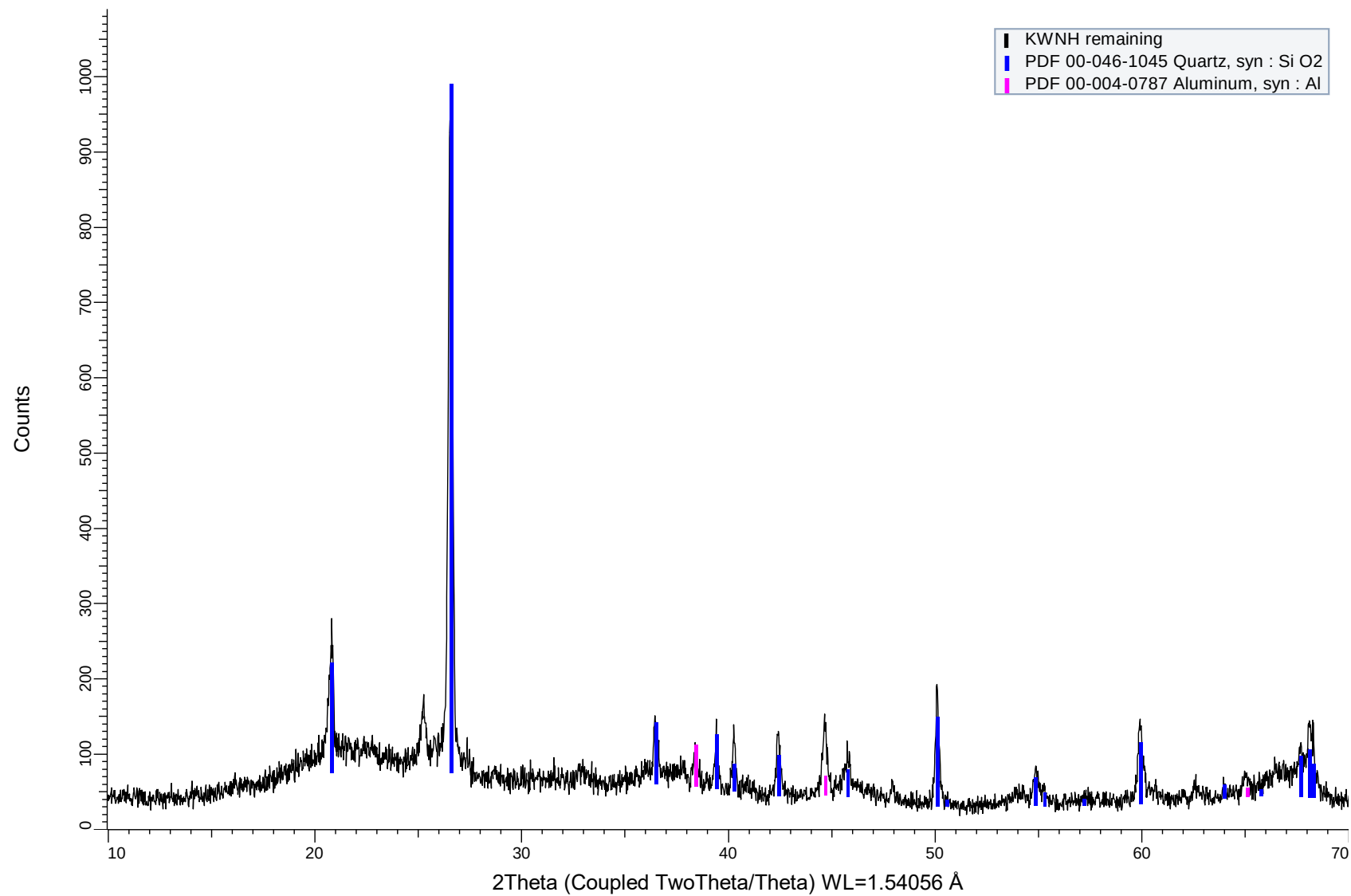
Some of the diffraction patterns include peaks that could not be positively identified (e.g. metakaolin). More data (e.g. slower XRD scans, analysis by SEM/TEM-EDS) may be required to complete the identification. If you have any suggestions of possible matches you would like me to check, just let me know.

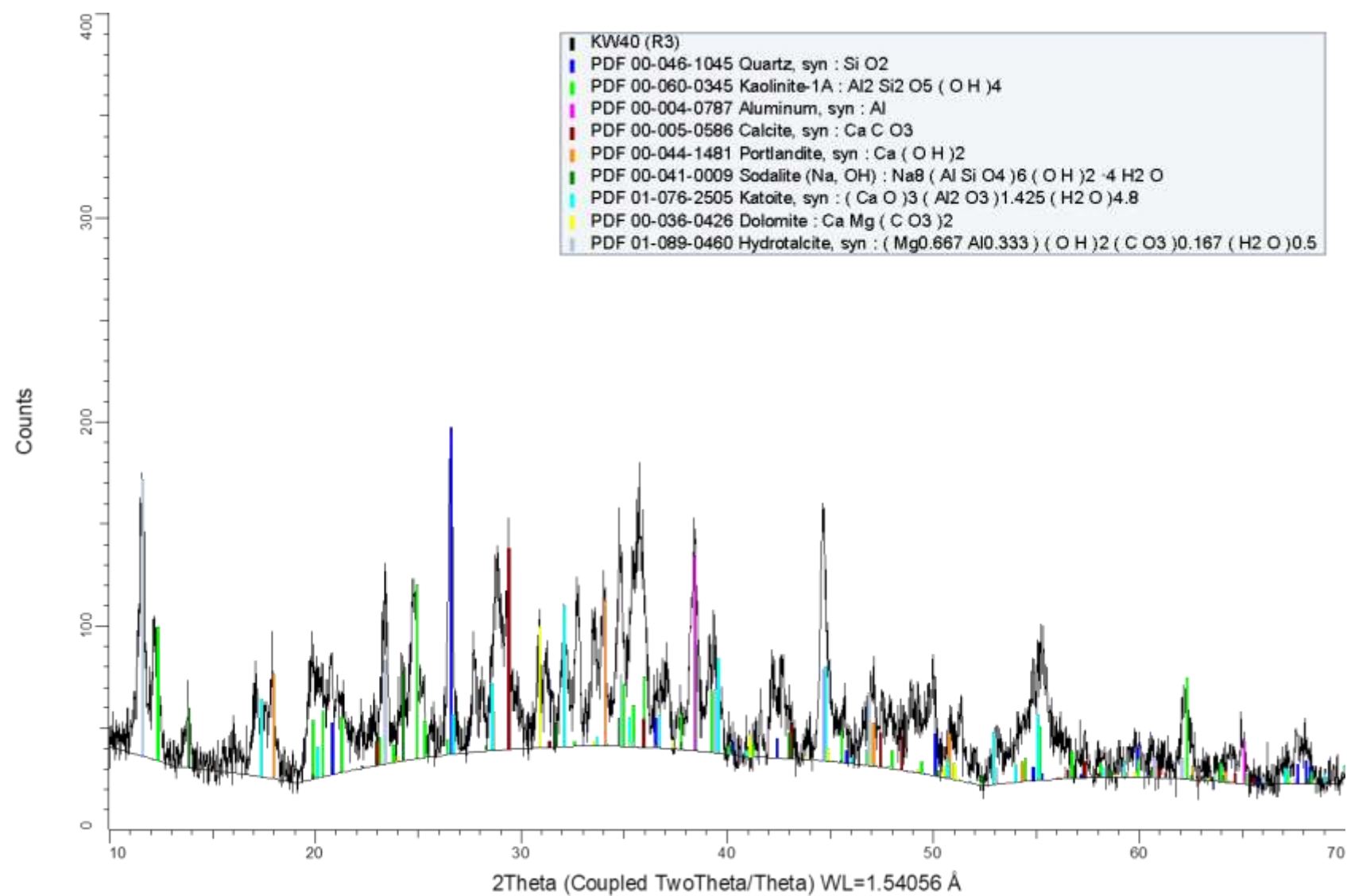


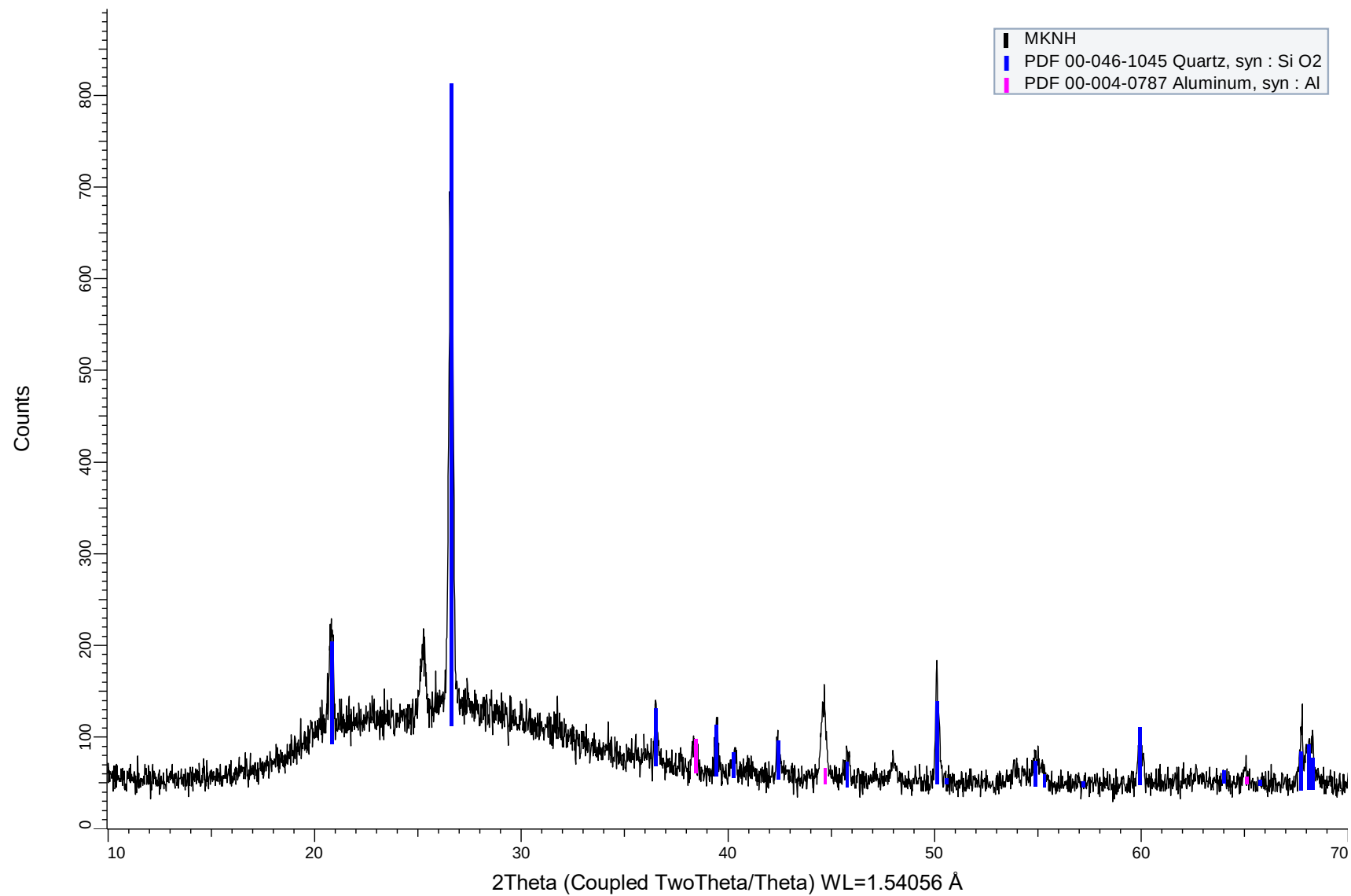


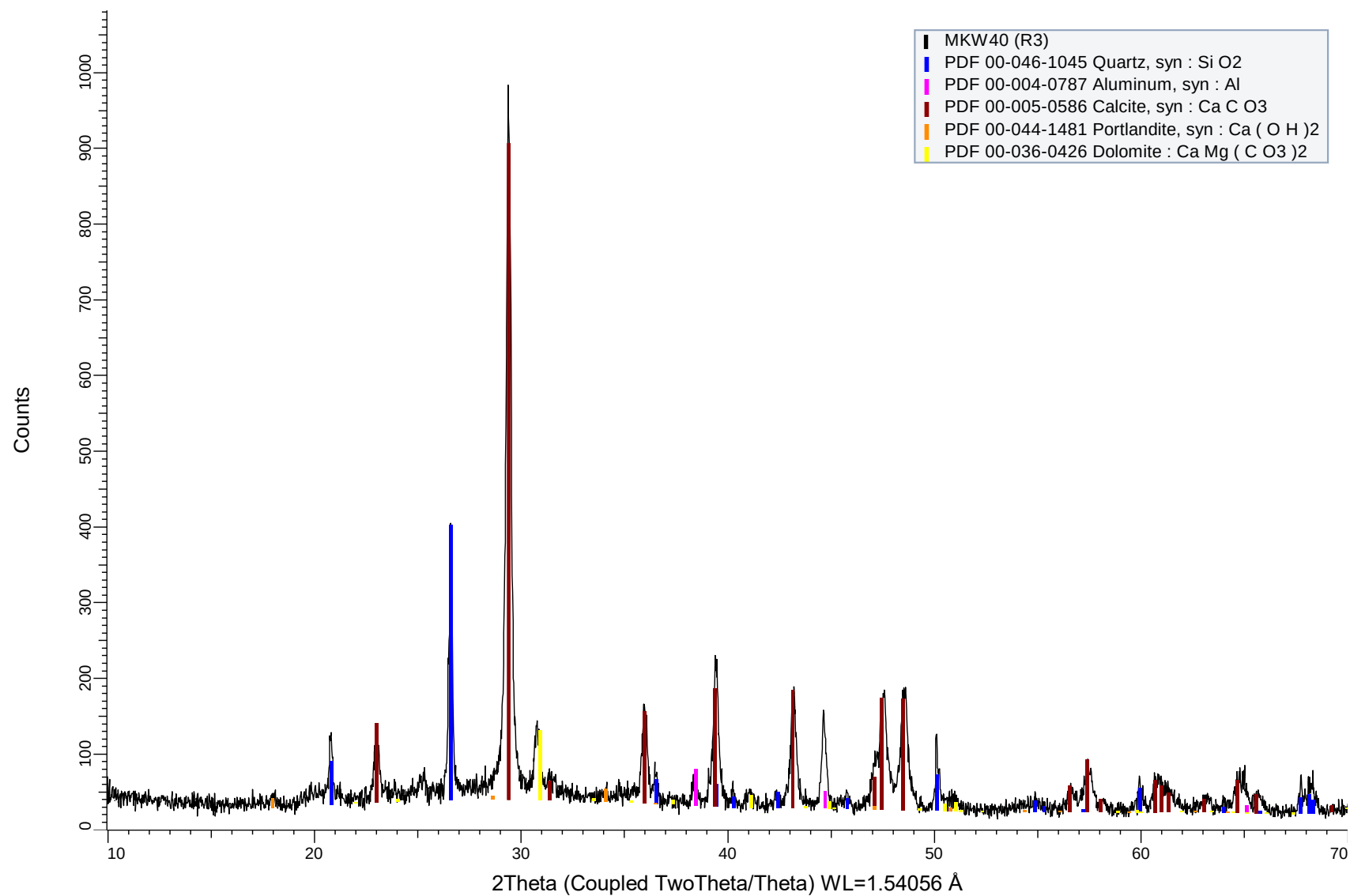


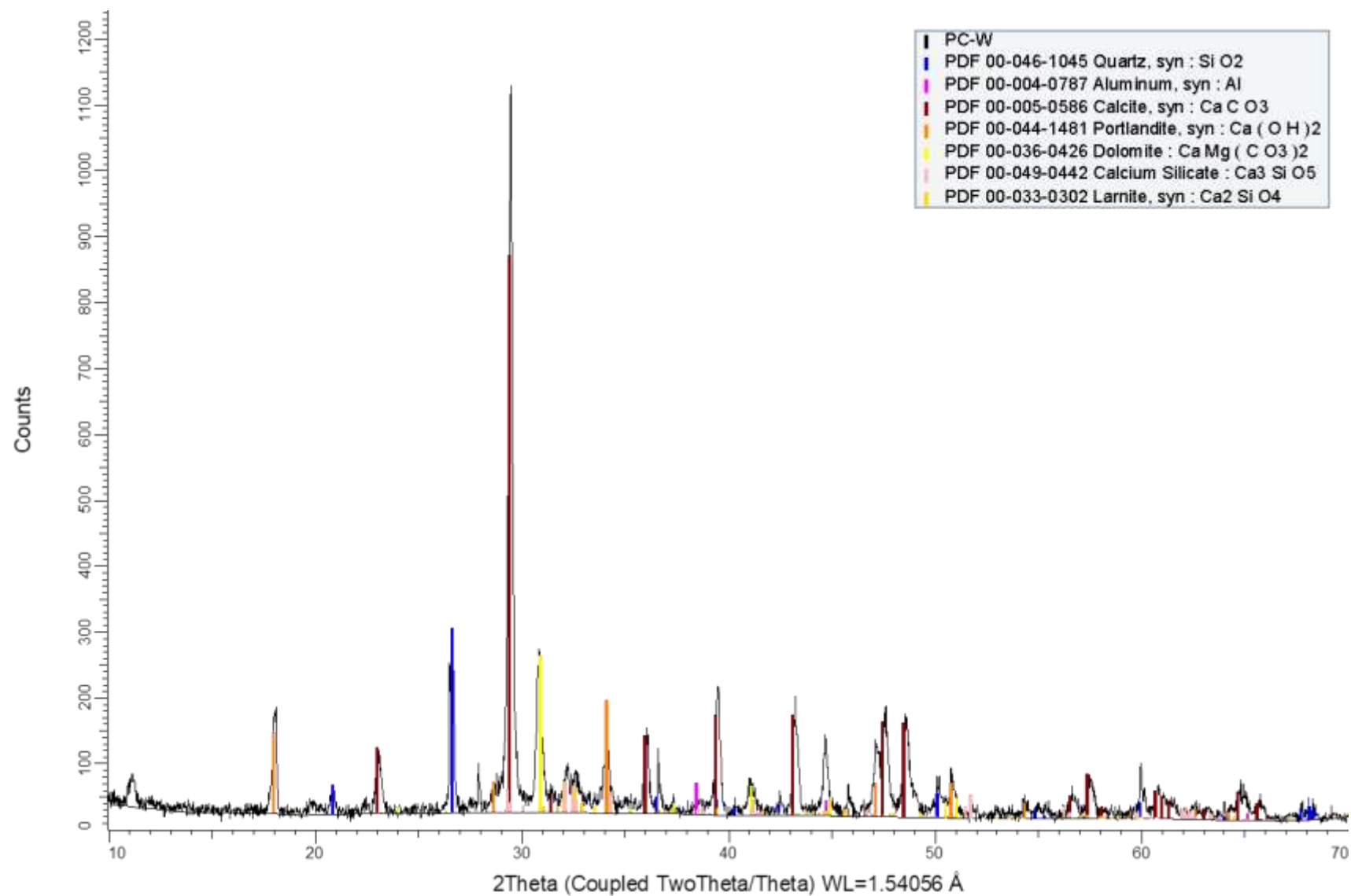


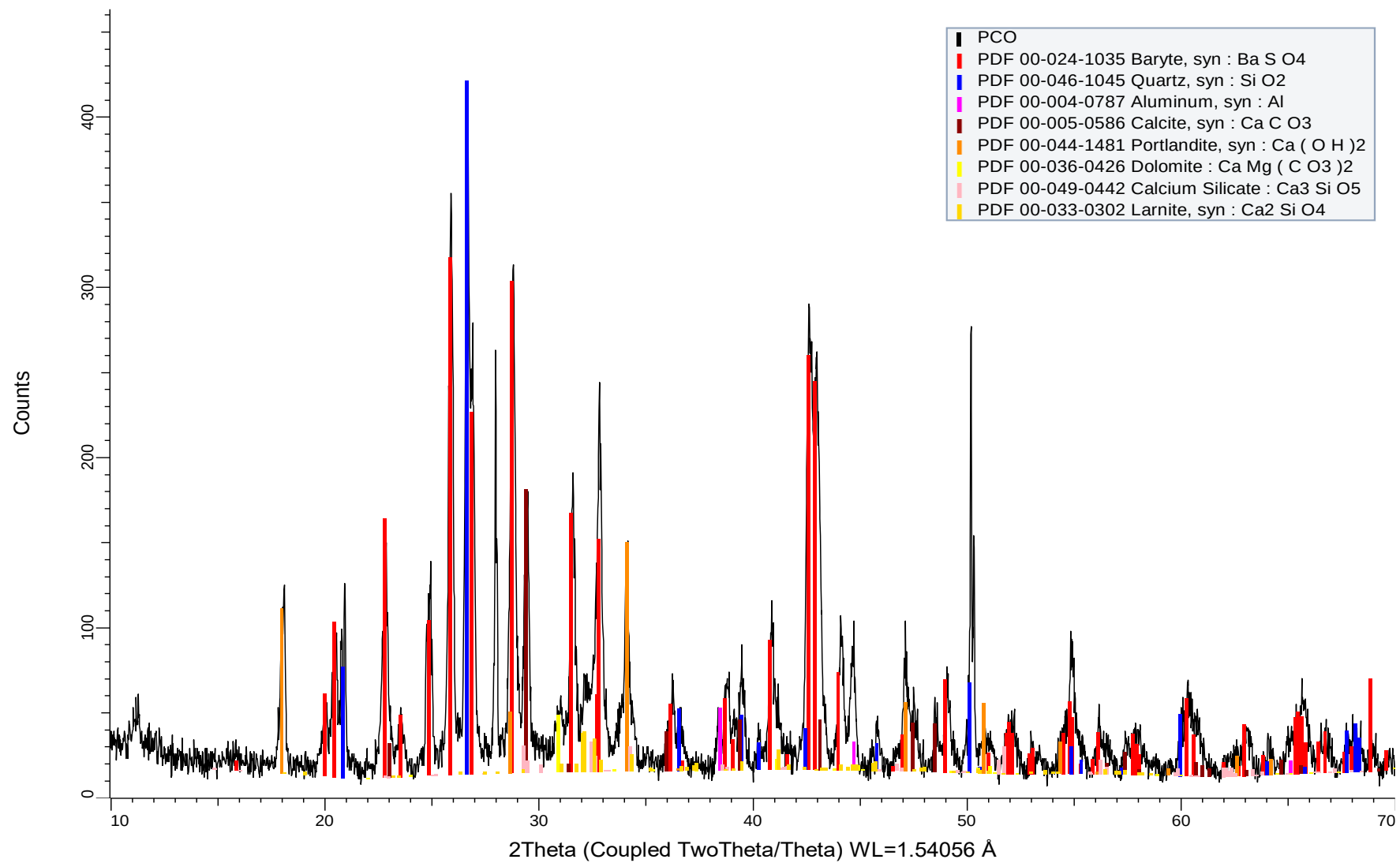






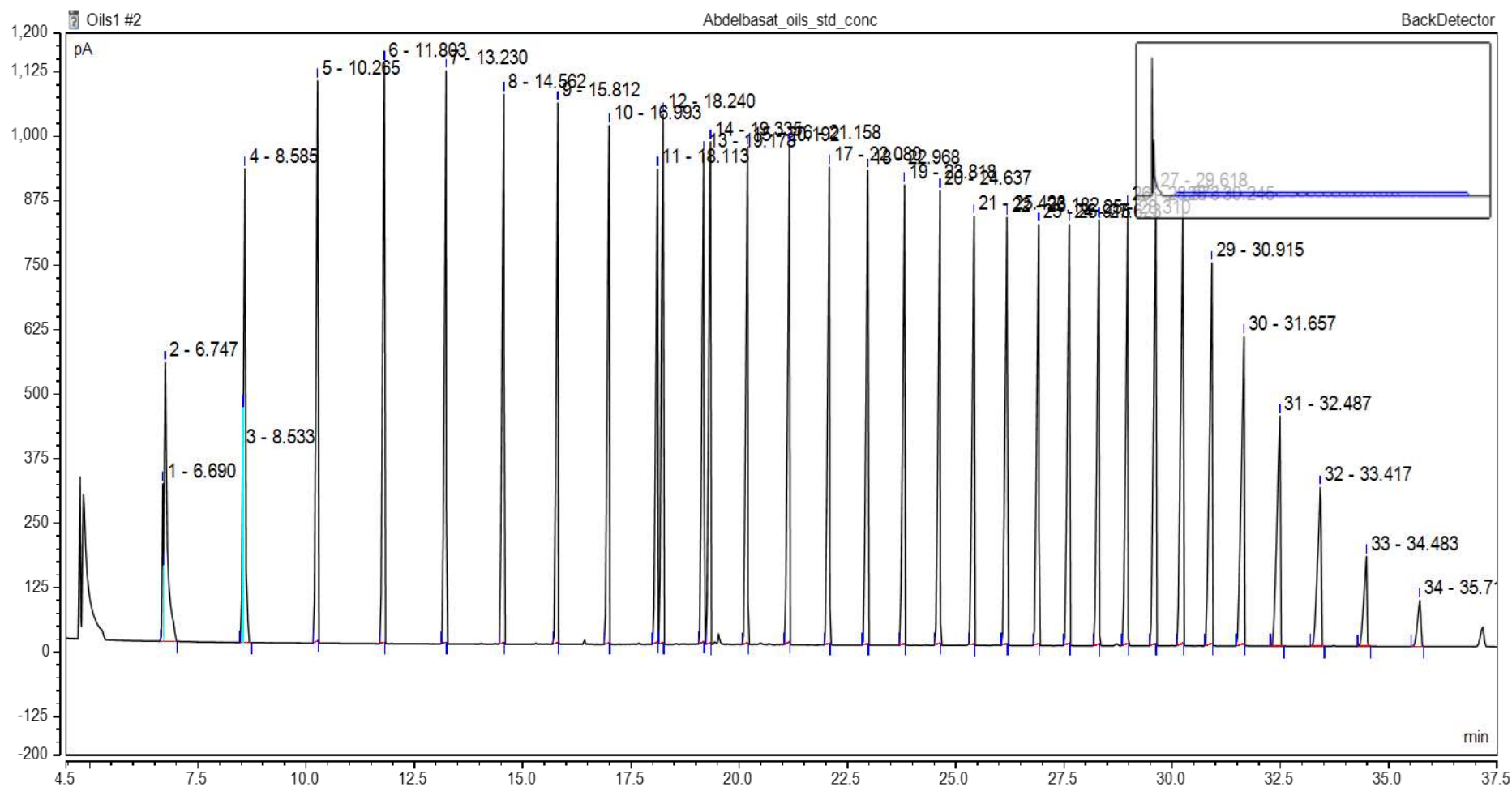




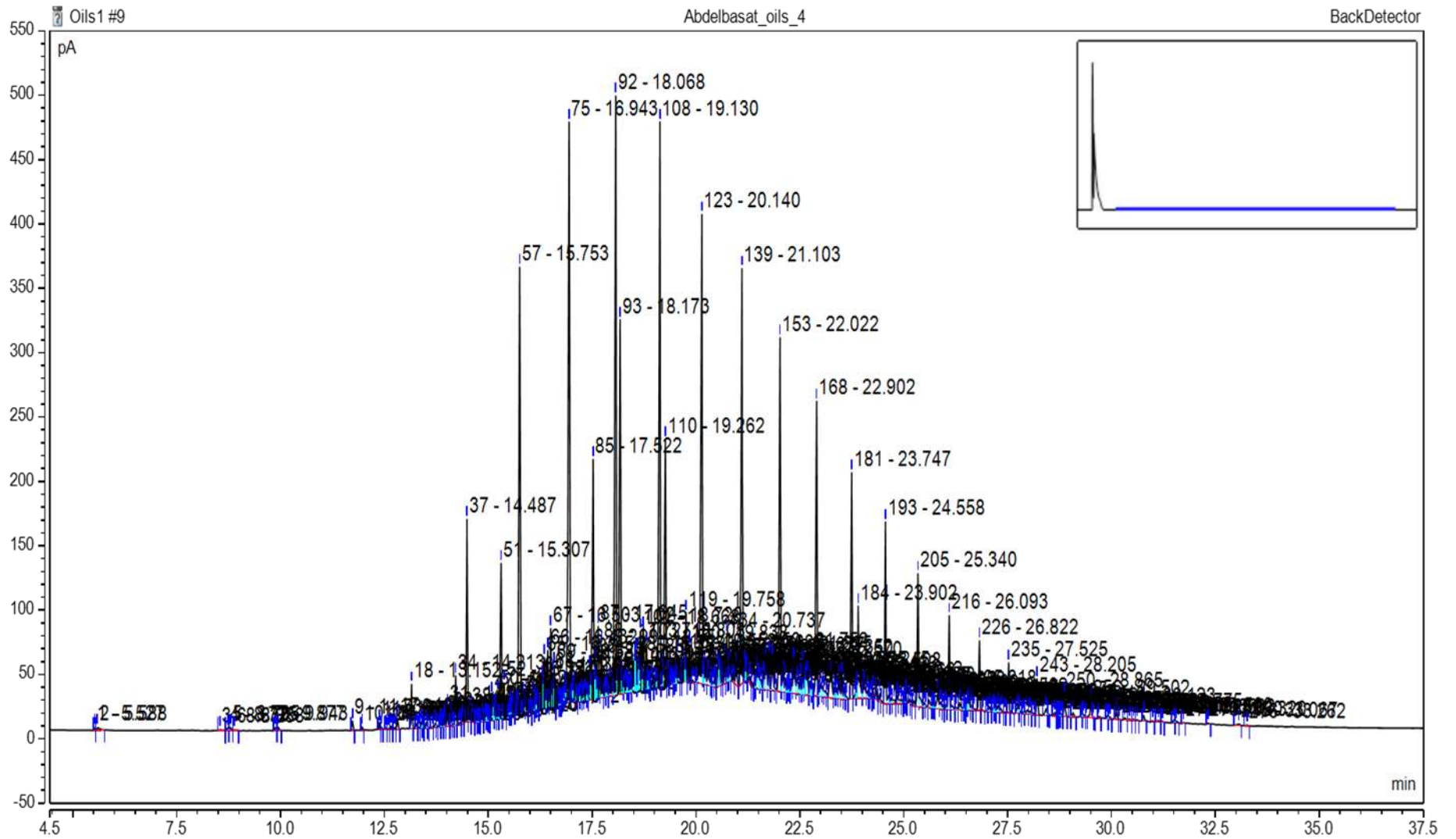


Appendix 3. GC-FID chromatograms for (S/S) through geopolymerisation approach

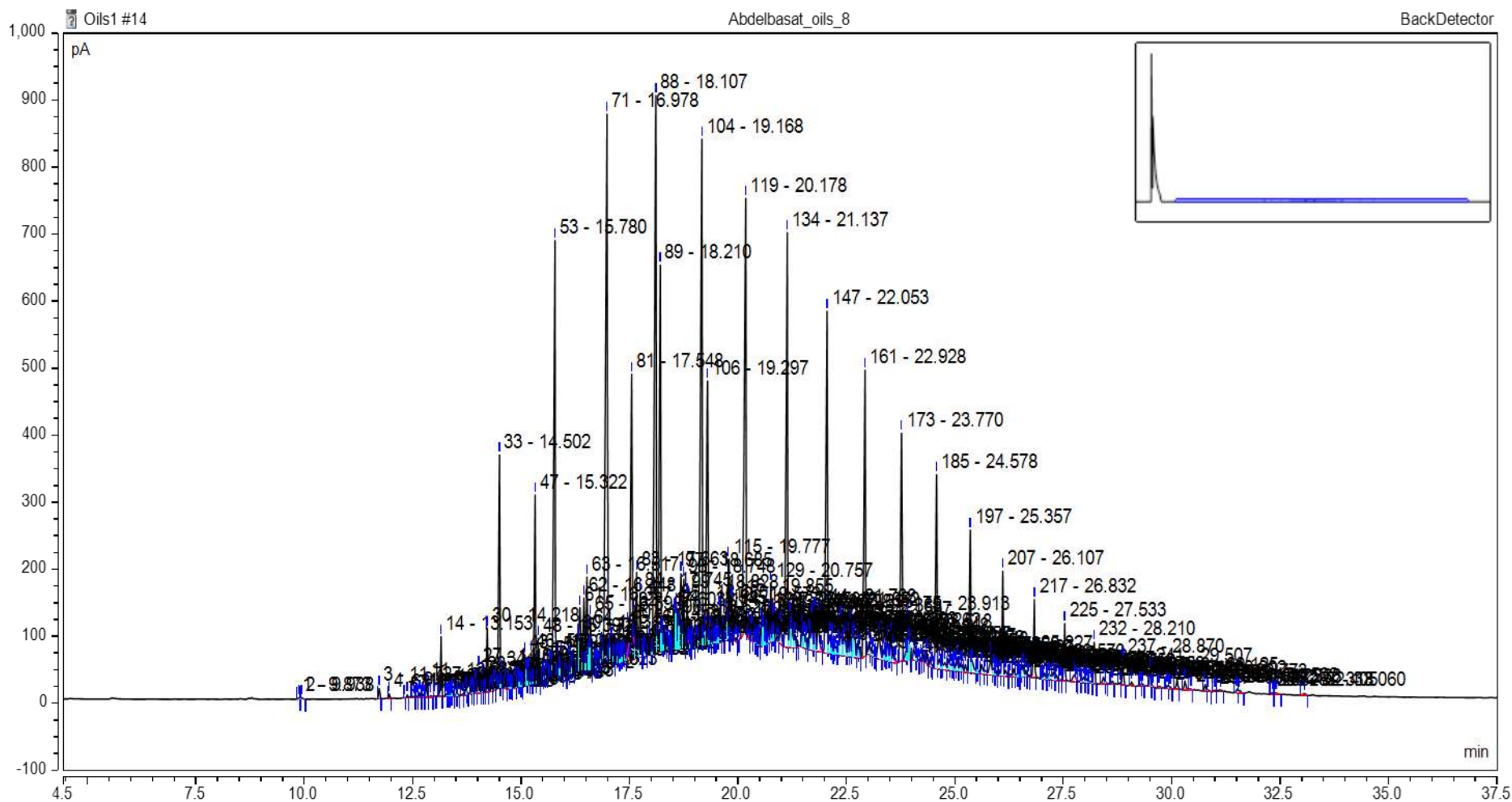
Oil Standard Reference Material (C8-C40)



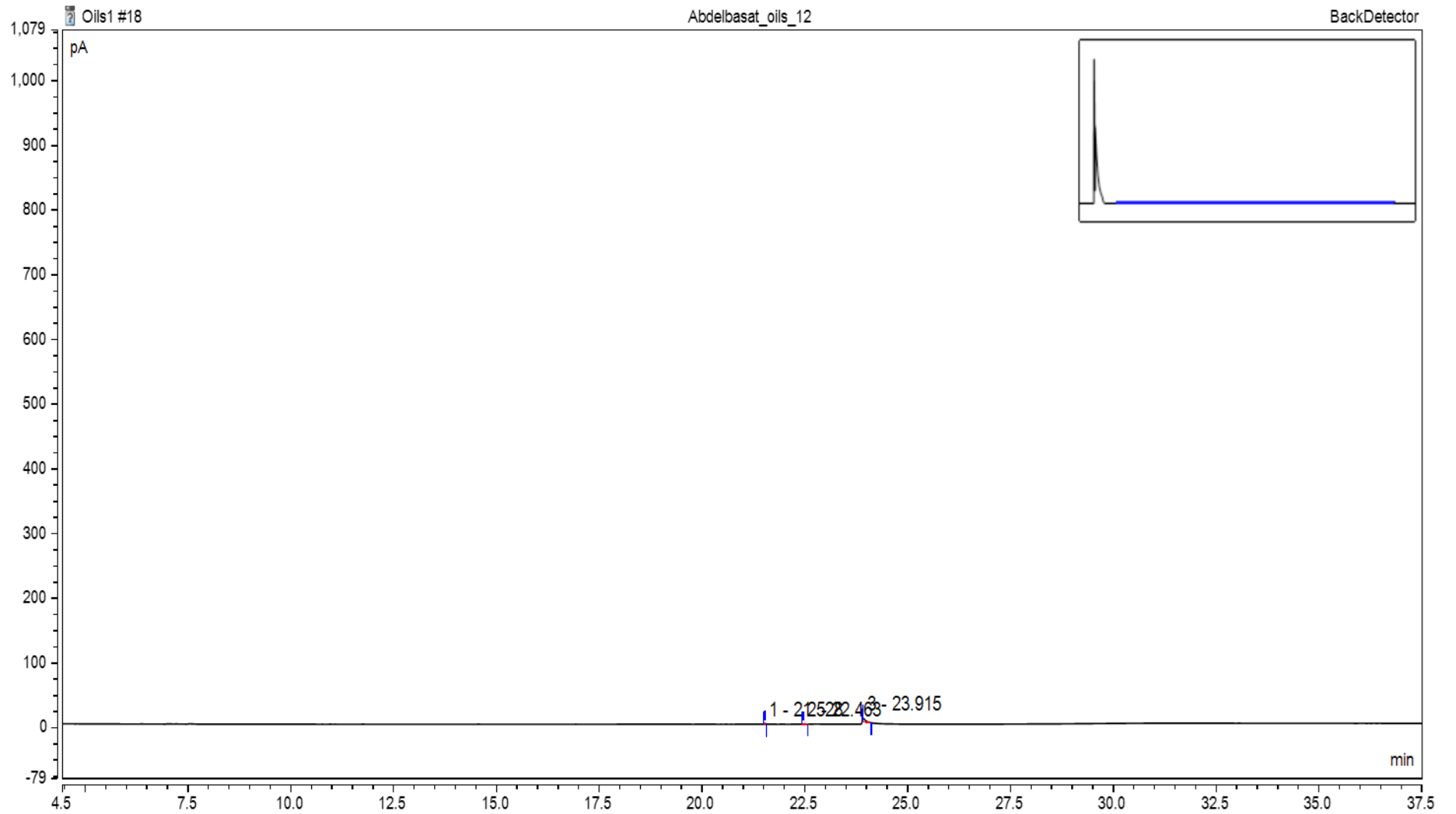
Water Based Mud Waste (Raw material)



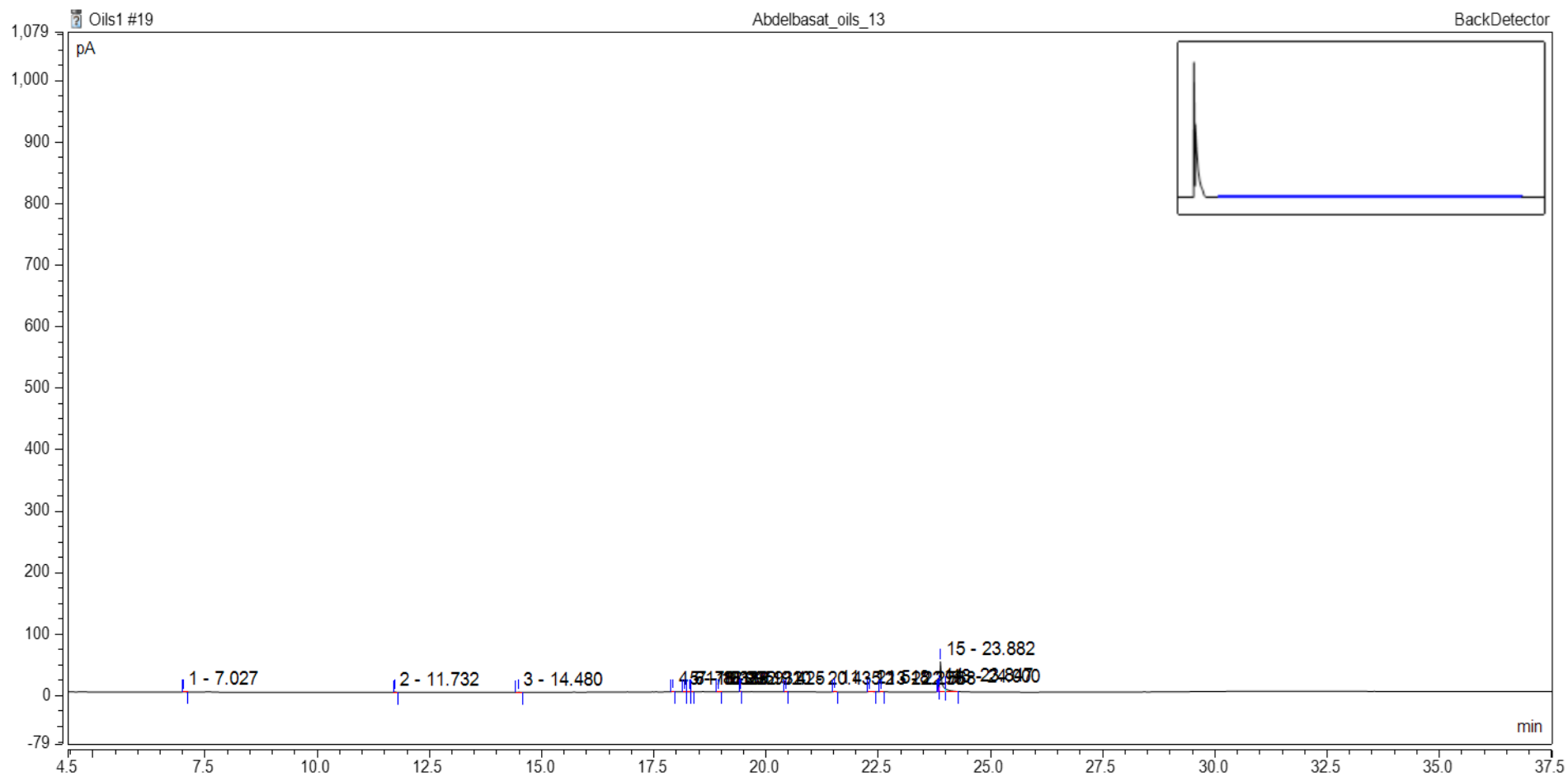
Oil Based Mud Waste (Raw material)



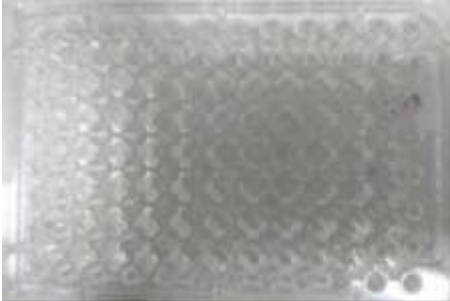
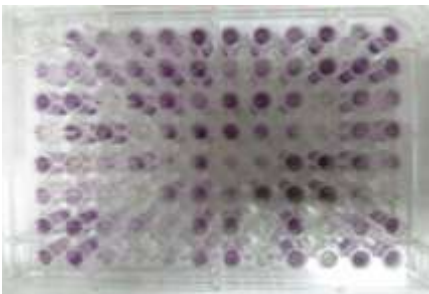
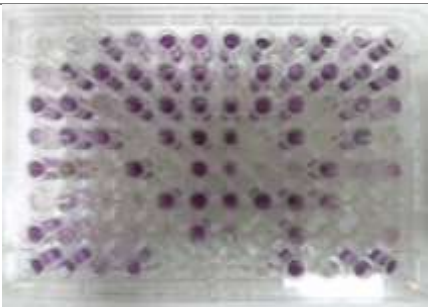
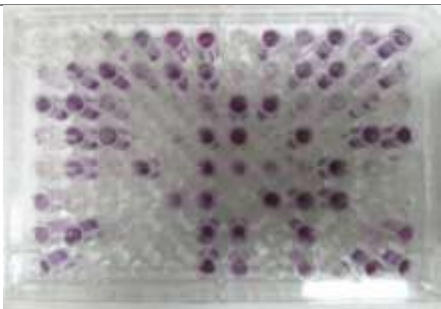
Recipe KW3 TPH leachate



Recipe KO3 TPH leachability



Appendix 4. Biolog plate analysis and calculations

Sample	Unplanted, unirrigated treatments	Planted, irrigated treatments
Control		
25-W		
50-W		

Measurement of AMR & CMD in treatment planted control

1	2	3	4	5	6	7	8	9	10	11	12
0.58	1.10	0.15	2.16	0.13	1.10	0.86	0.34	0.25	0.54	1.46	1.01
1.46	0.71	0.14	1.65	0.11	1.44	1.43	0.36	0.88	0.64	1.84	1.24
0.14	0.55	1.70	1.75	1.69	0.59	1.00	0.99	0.16	0.35	0.73	0.63
0.59	1.33	2.10	1.59	0.42	0.40	1.01	0.49	1.18	0.56	0.58	1.47
0.77	0.90	0.77	0.58	0.85	1.47	1.52	1.02	0.17	1.72	1.77	0.36
0.44	1.22	0.31	1.59	2.35	2.02	0.69	1.34	2.31	0.17	2.03	2.07
1.38	2.52	2.35	0.89	1.07	0.59	2.37	2.13	1.16	1.12	0.95	0.62
2.31	0.49	2.58	0.95	1.90	1.65	1.85	0.83	1.06	0.50	0.96	0.12
1	2	3	4	5	6	7	8	9	10	11	12
1.02	1.06	0.45	0.53	0.12	1.27	1.19	0.28	0.94	0.89	1.71	0.98
1.32	0.76	0.11	0.81	0.36	1.67	1.81	0.64	0.63	0.24	1.83	1.41
0.44	0.13	2.07	1.83	1.76	0.51	0.87	0.83	0.16	0.13	0.53	0.51
0.47	1.33	2.18	1.80	0.48	0.51	0.81	0.32	0.81	0.23	1.08	1.84
0.97	1.09	0.27	1.61	0.55	1.79	1.57	1.16	0.25	2.02	1.69	0.28
0.18	1.17	0.73	1.36	2.55	2.48	2.06	2.27	2.26	0.14	2.09	2.34
2.13	2.24	2.67	1.29	2.62	0.93	2.82	2.38	1.23	1.72	2.31	0.30
2.43	0.43	2.79	0.94	2.48	0.28	1.86	2.61	1.22	1.21	1.02	0.12
1	2	3	4	5	6	7	8	9	10	11	12
1.11	0.38	0.15	0.49	0.11	0.82	0.72	0.21	0.09	1.41	0.76	0.80
1.05	0.29	0.11	0.90	0.32	1.16	0.88	0.18	0.14	0.56	1.09	0.88
0.13	0.18	1.40	1.61	1.60	0.42	0.67	0.66	0.23	0.16	0.53	0.43
0.78	0.90	1.95	1.50	0.52	0.60	1.34	0.27	1.25	0.49	0.74	0.62
0.16	0.96	0.27	0.43	0.29	2.02	1.51	0.56	0.10	1.57	1.63	0.29
0.56	1.42	0.29	0.56	0.57	0.71	0.34	2.21	0.53	0.19	0.48	0.40
1.64	2.41	2.39	0.45	2.53	0.23	2.07	2.26	0.58	1.27	2.47	0.38
2.19	0.28	2.34	0.61	2.18	0.90	1.45	1.01	0.43	0.39	0.33	0.10

72 hours Average

0.90	0.85	0.25	1.06	0.12	1.07	0.92	0.28	0.43	0.95	1.31	0.93
1.27	0.58	0.12	1.12	0.27	1.42	1.37	0.39	0.55	0.48	1.59	1.18
0.23	0.29	1.72	1.73	1.68	0.50	0.84	0.82	0.18	0.21	0.60	0.52
0.61	1.19	2.08	1.63	0.47	0.50	1.05	0.36	1.08	0.43	0.80	1.31
0.63	0.98	0.44	0.87	0.56	1.76	1.53	0.92	0.17	1.77	1.69	0.31
0.39	1.27	0.44	1.17	1.83	1.74	1.03	1.94	1.70	0.17	1.53	1.60
1.72	2.39	2.47	0.88	2.07	0.58	2.42	2.26	0.99	1.37	1.91	0.43
2.31	0.40	2.57	0.83	2.19	0.95	1.72	1.48	0.91	0.70	0.77	0.11

0.00	0.00	0.00	0.16	0.00	0.17	0.02	0.00	0.00	0.05	0.41	0.03
0.37	0.00	0.00	0.22	0.00	0.52	0.47	0.00	0.00	0.00	0.69	0.27
0.00	0.00	0.82	0.83	0.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.29	1.18	0.73	0.00	0.00	0.15	0.00	0.18	0.00	0.00	0.41
0.00	0.08	0.00	0.00	0.00	0.86	0.63	0.01	0.00	0.87	0.79	0.00
0.00	0.37	0.00	0.27	0.92	0.83	0.13	1.04	0.80	0.00	0.63	0.70
0.81	1.49	1.57	0.00	1.17	0.00	1.52	1.36	0.09	0.47	1.01	0.00

1.41	0.00	1.67	0.00	1.29	0.04	0.82	0.58	0.00	0.00	0.00	0.00
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AWCD	33.0	AMR	0.35	CMD	38
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Measurement of AMR & CMD in treatment planted 25-W

1	2	3	4	5	6	7	8	9	10	11	12
0.41	1.23	1.74	2.08	1.63	2.08	2.46	2.65	1.99	3.01	2.38	2.90
0.71	2.70	2.32	1.51	2.69	2.86	1.24	2.73	1.41	2.94	1.98	1.88
2.61	2.73	0.96	2.65	2.59	2.77	2.42	2.81	2.37	1.90	1.90	0.65
0.65	2.37	1.35	0.77	1.05	2.03	2.14	1.79	2.00	0.61	1.05	2.23
2.32	1.76	1.10	2.00	0.44	1.40	1.01	1.39	1.63	1.98	2.06	0.99
0.69	1.08	0.55	0.63	1.79	1.44	1.23	2.17	2.12	2.50	0.77	0.76
2.09	1.36	0.93	0.68	0.70	1.72	2.17	1.72	0.88	0.59	1.08	1.17
1.53	1.98	1.63	1.27	0.33	0.93	1.31	0.36	1.86	0.49	1.31	2.07

1	2	3	4	5	6	7	8	9	10	11	12
0.30	0.21	1.65	1.05	1.97	1.32	2.59	2.68	0.80	2.96	0.80	2.84
0.70	2.70	2.19	2.40	2.69	2.69	0.76	2.65	1.17	2.84	2.37	2.65
2.61	2.62	0.57	2.63	2.64	2.41	2.68	2.71	1.64	0.42	1.03	0.72
0.74	2.47	1.36	0.27	1.31	2.14	2.26	0.34	2.12	0.30	1.14	0.22
2.32	1.45	0.28	2.08	0.24	1.31	1.00	0.50	0.69	1.40	0.56	0.57
0.38	0.95	0.56	0.38	1.71	1.65	1.96	2.16	1.46	0.93	0.28	0.16
1.65	0.94	0.54	0.52	0.49	1.68	0.61	0.24	1.46	0.20	0.22	0.59
1.75	1.75	0.88	1.23	0.39	0.26	0.11	0.29	1.73	0.27	1.28	1.50

1	2	3	4	5	6	7	8	9	10	11	12
0.22	0.26	0.74	1.04	1.73	0.98	0.65	0.74	0.85	0.94	0.81	0.93
0.59	0.58	0.32	0.91	0.49	0.65	0.76	0.47	0.56	0.81	0.82	0.83
0.72	0.57	0.74	0.55	1.02	0.66	1.02	0.86	0.81	0.71	0.74	0.63
0.53	2.16	1.66	0.22	0.24	2.46	1.19	0.22	1.12	0.60	0.73	0.22
0.81	0.94	0.26	1.38	0.21	0.88	1.17	0.79	2.09	2.17	0.49	0.51
0.39	0.25	0.28	0.20	0.73	1.20	0.94	1.65	2.36	1.37	0.22	0.25
0.81	0.87	0.59	0.49	0.37	1.13	1.84	0.23	1.78	0.22	0.38	0.06
0.71	0.14	0.58	0.19	0.32	0.31	0.24	0.22	0.50	0.16	0.72	0.74

72 Hours Average

0.31	0.57	1.37	1.39	1.77	1.46	1.90	2.03	1.21	2.30	1.33	2.22
0.67	1.99	1.61	1.61	1.96	2.07	0.92	1.95	1.05	2.20	1.72	1.79
1.98	1.97	0.76	1.94	2.08	1.95	2.04	2.13	1.61	1.01	1.22	0.67
0.64	2.34	1.46	0.42	0.87	2.21	1.86	0.78	1.74	0.50	0.98	0.89
1.81	1.38	0.54	1.82	0.30	1.20	1.06	0.89	1.47	1.85	1.04	0.69
0.49	0.76	0.47	0.40	1.41	1.43	1.37	2.00	1.98	1.60	0.42	0.39
1.51	1.05	0.69	0.56	0.52	1.51	1.54	0.73	1.37	0.34	0.56	0.60
1.33	1.29	1.03	0.90	0.35	0.50	0.55	0.29	1.36	0.31	1.10	1.43

0.00	0.25	1.06	1.08	1.46	1.15	1.59	1.71	0.90	1.99	1.02	1.91
0.36	1.68	1.30	1.29	1.64	1.76	0.61	1.64	0.73	1.88	1.41	1.48
1.67	1.66	0.44	1.63	1.77	1.63	1.73	1.82	1.29	0.70	0.91	0.36
0.32	2.02	1.14	0.11	0.55	1.90	1.55	0.47	1.43	0.19	0.66	0.58
1.50	1.07	0.23	1.51	0.00	0.88	0.75	0.58	1.15	1.54	0.72	0.37
0.17	0.45	0.15	0.09	1.10	1.11	1.06	1.68	1.67	1.29	0.11	0.08
1.20	0.74	0.38	0.25	0.21	1.20	1.23	0.42	1.06	0.03	0.25	0.29
1.02	0.98	0.72	0.58	0.03	0.19	0.24	0.00	1.05	0.00	0.79	1.12

AWCD	89.64	AMR	0.94	CMD	75
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Measurement of AMR & CMD in treatment planted 50-W

1	2	3	4	5	6	7	8	9	10	11	12
0.45	0.49	0.99	1.95	1.22	2.19	0.45	2.38	1.04	2.40	0.93	2.78
0.73	2.43	2.27	1.55	2.69	2.74	0.79	0.78	1.53	2.87	1.33	2.24
2.61	2.67	1.04	0.76	0.74	1.05	2.61	2.80	0.90	0.89	0.95	0.48
0.62	2.41	2.02	0.48	0.69	2.39	1.98	0.48	2.48	0.48	2.04	1.75
0.76	1.88	0.65	2.24	0.62	2.03	0.95	0.77	0.75	2.44	0.73	0.05
0.84	0.47	0.61	0.38	1.21	1.63	0.60	2.31	1.96	2.34	0.38	0.39
1.10	2.41	0.72	0.57	0.57	2.46	2.09	0.50	2.29	0.48	0.78	1.46
1.35	0.35	0.28	0.33	0.44	1.76	1.16	0.37	1.10	0.45	1.79	1.60
1	2	3	4	5	6	7	8	9	10	11	12
0.52	0.50	0.86	1.12	2.08	2.41	0.44	0.66	0.89	1.12	0.94	1.24
0.68	0.96	0.44	1.33	0.85	2.53	0.87	0.72	0.56	2.84	1.31	0.96
0.92	1.12	0.73	0.71	0.79	0.87	1.01	1.04	1.03	0.96	1.29	0.39
0.65	2.63	2.44	0.41	0.35	2.39	2.24	0.58	2.50	0.44	2.35	1.89
0.90	1.64	0.64	1.57	0.41	2.05	0.78	0.83	1.11	2.29	0.65	1.27
0.81	0.60	0.47	0.28	1.38	2.21	0.40	2.44	2.43	2.62	0.52	0.29
2.18	2.58	0.67	0.80	0.57	2.30	1.90	0.51	0.05	0.44	1.17	2.45
0.22	0.15	0.15	0.20	0.26	1.52	0.14	0.11	0.05	0.25	0.19	0.37
1	2	3	4	5	6	7	8	9	10	11	12
0.51	0.78	1.14	2.23	1.70	1.61	2.20	2.24	2.81	2.23	2.35	1.21
1.24	2.26	0.83	1.81	2.76	2.37	1.75	1.27	0.50	2.66	1.73	2.14
2.40	2.63	0.94	2.65	2.19	2.74	1.11	2.93	1.04	2.34	2.21	0.72
0.84	2.30	2.57	0.52	1.87	2.49	1.86	2.31	2.30	0.58	1.86	1.69
1.90	1.91	1.23	2.48	1.58	2.21	0.93	1.23	2.07	2.45	1.73	0.97
0.99	1.10	0.49	0.51	2.05	1.91	1.01	2.18	2.57	2.42	0.53	0.43
1.31	2.38	0.96	1.06	0.89	2.28	1.58	2.11	2.30	1.01	0.83	1.46
1.62	1.55	0.63	1.90	1.03	1.58	1.39	0.49	1.93	0.61	1.24	1.00

72 hours Average

1	2	3	4	5	6	7	8	9	10	11	12
0.49	0.59	1.00	1.77	1.67	2.07	1.03	1.76	1.58	1.92	1.41	1.74
0.88	1.88	1.18	1.56	2.10	2.55	1.13	0.92	0.86	2.79	1.46	1.78
1.98	2.14	0.90	1.37	1.24	1.55	1.57	2.25	0.99	1.40	1.48	0.53
0.70	2.45	2.34	0.47	0.97	2.43	2.03	1.13	2.43	0.50	2.08	1.78

1.19	1.81	0.84	2.09	0.87	2.10	0.89	0.94	1.31	2.39	1.04	0.77
0.88	0.72	0.52	0.39	1.55	1.92	0.67	2.31	2.32	2.46	0.48	0.37
1.53	2.46	0.78	0.81	0.68	2.35	1.86	1.04	1.55	0.64	0.92	1.79
1.06	0.69	0.35	0.81	0.58	1.62	0.90	0.32	1.03	0.44	1.07	0.99

0.00	0.10	0.50	1.27	1.17	1.58	0.53	1.27	1.09	1.43	0.91	1.25
0.39	1.39	0.68	1.07	1.61	2.05	0.64	0.43	0.37	2.30	0.96	1.29
1.48	1.65	0.41	0.88	0.75	1.06	1.08	1.76	0.49	0.90	0.99	0.04
0.21	1.95	1.85	0.00	0.48	1.93	1.53	0.63	1.94	0.01	1.59	1.28
0.70	1.32	0.35	1.60	0.38	1.60	0.40	0.45	0.81	1.90	0.54	0.27
0.39	0.23	0.03	0.00	1.05	1.43	0.18	1.81	1.83	1.97	0.00	0.00
1.03	1.96	0.29	0.32	0.18	1.85	1.36	0.55	1.05	0.15	0.43	1.30
0.57	0.19	0.00	0.31	0.08	1.13	0.40	0.00	0.53	0.00	0.58	0.50

AWCD	83.2	AMR	0.88	CMD	77
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Measurement of AMR & CMD in treatment unplanted control

1	2	3	4	5	6	7	8	9	10	11	12
0.45	0.49	0.99	1.95	1.22	2.19	0.45	2.38	1.04	2.40	0.93	2.78
0.73	2.43	2.27	1.55	2.69	2.74	0.79	0.78	1.53	2.87	1.33	2.24
2.61	2.67	1.04	0.76	0.74	1.05	2.61	2.80	0.90	0.89	0.95	0.48
0.62	2.41	2.02	0.48	0.69	2.39	1.98	0.48	2.48	0.48	2.04	1.75
0.76	1.88	0.65	2.24	0.62	2.03	0.95	0.77	0.75	2.44	0.73	0.05
0.84	0.47	0.61	0.38	1.21	1.63	0.60	2.31	1.96	2.34	0.38	0.39
1.10	2.41	0.72	0.57	0.57	2.46	2.09	0.50	2.29	0.48	0.78	1.46
1.35	0.35	0.28	0.33	0.44	1.76	1.16	0.37	1.10	0.45	1.79	1.60
1	2	3	4	5	6	7	8	9	10	11	12
0.52	0.50	0.86	1.12	2.08	2.41	0.44	0.66	0.89	1.12	0.94	1.24
0.68	0.96	0.44	1.33	0.85	2.53	0.87	0.72	0.56	2.84	1.31	0.96
0.92	1.12	0.73	0.71	0.79	0.87	1.01	1.04	1.03	0.96	1.29	0.39
0.65	2.63	2.44	0.41	0.35	2.39	2.24	0.58	2.50	0.44	2.35	1.89
0.90	1.64	0.64	1.57	0.41	2.05	0.78	0.83	1.11	2.29	0.65	1.27
0.81	0.60	0.47	0.28	1.38	2.21	0.40	2.44	2.43	2.62	0.52	0.29
2.18	2.58	0.67	0.80	0.57	2.30	1.90	0.51	0.05	0.44	1.17	2.45
0.22	0.15	0.15	0.20	0.26	1.52	0.14	0.11	0.05	0.25	0.19	0.37
1	2	3	4	5	6	7	8	9	10	11	12
0.51	0.78	1.14	2.23	1.70	1.61	2.20	2.24	2.81	2.23	2.35	1.21
1.24	2.26	0.83	1.81	2.76	2.37	1.75	1.27	0.50	2.66	1.73	2.14
2.40	2.63	0.94	2.65	2.19	2.74	1.11	2.93	1.04	2.34	2.21	0.72
0.84	2.30	2.57	0.52	1.87	2.49	1.86	2.31	2.30	0.58	1.86	1.69
1.90	1.91	1.23	2.48	1.58	2.21	0.93	1.23	2.07	2.45	1.73	0.97
0.99	1.10	0.49	0.51	2.05	1.91	1.01	2.18	2.57	2.42	0.53	0.43
1.31	2.38	0.96	1.06	0.89	2.28	1.58	2.11	2.30	1.01	0.83	1.46
1.62	1.55	0.63	1.90	1.03	1.58	1.39	0.49	1.93	0.61	1.24	1.00

0.49	0.59	1.00	1.77	1.67	2.07	1.03	1.76	1.58	1.92	1.41	1.74
0.88	1.88	1.18	1.56	2.10	2.55	1.13	0.92	0.86	2.79	1.46	1.78
1.98	2.14	0.90	1.37	1.24	1.55	1.57	2.25	0.99	1.40	1.48	0.53
0.70	2.45	2.34	0.47	0.97	2.43	2.03	1.13	2.43	0.50	2.08	1.78
1.19	1.81	0.84	2.09	0.87	2.10	0.89	0.94	1.31	2.39	1.04	0.77
0.88	0.72	0.52	0.39	1.55	1.92	0.67	2.31	2.32	2.46	0.48	0.37
1.53	2.46	0.78	0.81	0.68	2.35	1.86	1.04	1.55	0.64	0.92	1.79
1.06	0.69	0.35	0.81	0.58	1.62	0.90	0.32	1.03	0.44	1.07	0.99

0.00	0.10	0.50	1.27	1.17	1.58	0.53	1.27	1.09	1.43	0.91	1.25
0.39	1.39	0.68	1.07	1.61	2.05	0.64	0.43	0.37	2.30	0.96	1.29
1.48	1.65	0.41	0.88	0.75	1.06	1.08	1.76	0.49	0.90	0.99	0.04
0.21	1.95	1.85	0.00	0.48	1.93	1.53	0.63	1.94	0.01	1.59	1.28
0.70	1.32	0.35	1.60	0.38	1.60	0.40	0.45	0.81	1.90	0.54	0.27
0.39	0.23	0.03	0.00	1.05	1.43	0.18	1.81	1.83	1.97	0.00	0.00
1.03	1.96	0.29	0.32	0.18	1.85	1.36	0.55	1.05	0.15	0.43	1.30
0.57	0.19	0.00	0.31	0.08	1.13	0.40	0.00	0.53	0.00	0.58	0.50

AWCD	83.15	AMR	0.88	CMD	77
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Measurement of AMR & CMD in treatment unplanted 25-W

1	2	3	4	5	6	7	8	9	10	11	12
1.02	1.00	1.00	1.01	0.98	1.01	1.00	0.99	0.99	1.02	0.90	0.92
1.00	1.08	1.03	1.06	1.07	1.03	1.07	1.03	1.09	1.00	1.05	0.92
1.02	1.08	1.08	1.06	1.06	1.05	1.06	1.05	1.08	0.99	0.99	1.01
1.29	1.04	1.06	1.05	1.00	1.07	1.04	1.06	1.08	1.13	1.05	0.95
1.03	1.04	1.16	1.04	1.16	1.14	0.99	1.14	0.96	0.97	0.99	0.92
1.08	1.03	1.01	1.00	1.05	1.08	1.05	0.98	1.00	0.92	0.98	0.89
0.99	1.08	1.04	0.99	1.06	1.00	1.02	1.02	0.98	1.00	0.80	0.92
0.98	0.98	0.94	0.96	0.92	0.94	0.94	0.38	0.91	0.91	0.82	0.91
1	2	3	4	5	6	7	8	9	10	11	12
0.89	0.82	0.82	0.99	0.79	0.96	0.90	0.93	0.92	1.00	0.86	0.91
1.00	0.97	0.99	1.05	1.02	1.03	1.01	1.00	1.03	1.00	0.91	0.94
0.95	0.98	0.98	1.08	1.05	1.00	0.98	1.01	0.99	0.97	0.89	1.13
0.87	1.04	1.01	1.10	1.08	1.06	1.04	1.04	0.96	0.98	1.06	1.07
0.99	1.01	1.05	1.01	0.94	0.97	1.03	1.06	1.00	0.96	0.95	0.92
0.97	0.95	1.00	0.95	1.05	1.06	0.99	1.03	1.03	0.88	0.96	0.84
0.94	1.00	0.83	1.02	1.01	0.99	1.00	1.03	1.00	0.94	0.90	0.87
0.94	0.96	0.93	0.97	1.07	0.92	0.91	0.94	0.94	1.06	0.89	0.88
1	2	3	4	5	6	7	8	9	10	11	12
0.89	0.98	0.94	0.93	0.89	0.96	0.90	0.89	0.92	0.88	0.79	0.86

0.97	0.97	0.89	0.99	0.99	0.92	0.92	0.95	0.94	0.91	0.88	0.85
0.98	0.96	0.97	0.95	0.99	0.94	0.89	1.05	0.98	0.88	0.86	0.85
1.09	0.91	0.89	1.00	0.97	0.97	0.97	0.89	1.05	1.01	0.88	0.84
0.93	0.88	0.94	0.92	0.94	0.83	0.88	0.86	0.94	0.88	0.88	0.85
0.97	0.88	0.85	0.89	0.84	0.85	0.88	0.93	0.87	0.91	0.83	0.81
0.05	0.98	1.07	0.92	0.88	0.83	0.87	0.89	0.94	0.88	0.83	0.85
0.85	0.89	0.85	0.86	0.88	0.85	0.85	0.79	0.80	0.80	0.83	0.84

72 hours Average

0.93	0.93	0.92	0.98	0.89	0.98	0.93	0.94	0.94	0.97	0.85	0.90
0.99	1.01	0.97	1.04	1.03	1.00	1.00	0.99	1.02	0.97	0.95	0.91
0.98	1.01	1.01	1.03	1.03	1.00	0.98	1.04	1.01	0.94	0.92	1.00
1.08	0.99	0.98	1.05	1.02	1.03	1.02	1.00	1.03	1.04	1.00	0.95
0.98	0.97	1.05	0.99	1.01	0.98	0.96	1.02	0.97	0.94	0.94	0.90
1.01	0.95	0.95	0.94	0.98	1.00	0.97	0.98	0.97	0.90	0.92	0.85
0.66	1.02	0.98	0.98	0.98	0.94	0.96	0.98	0.98	0.94	0.84	0.88
0.92	0.95	0.90	0.93	0.96	0.90	0.90	0.71	0.88	0.92	0.85	0.87

0.00	0.00	0.00	0.04	0.00	0.04	0.00	0.00	0.01	0.04	0.00	0.00
0.06	0.08	0.04	0.10	0.09	0.06	0.07	0.06	0.09	0.04	0.01	0.00
0.05	0.07	0.08	0.10	0.10	0.07	0.05	0.10	0.08	0.01	0.00	0.06
0.15	0.06	0.05	0.12	0.08	0.10	0.08	0.06	0.10	0.11	0.06	0.02
0.05	0.04	0.12	0.06	0.08	0.05	0.03	0.08	0.03	0.01	0.01	0.00
0.08	0.02	0.02	0.01	0.05	0.06	0.04	0.05	0.03	0.00	0.00	0.00
0.00	0.09	0.04	0.05	0.05	0.01	0.03	0.05	0.04	0.01	0.00	0.00
0.00	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00

AWCD	3.91	AMR	0.04	CMD	0
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