Wastewater Treatment Using
Mineral-Based Materials

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Abstract

Human activities unintentionally add pollutants to water bodies. This research has focused on the removal of trace elements from sources of water pollution (point and non-point), using a mineral based by-product (Blueguard® solids). The materials were characterised to identify the mineralogy, structure, porosity, and composition using different techniques including X-ray Fluorescence Spectrometry, X-ray Powder Diffraction and Brunauer–Emmett–Teller gas sorption methods. The results showed that the main compounds of the Blueguard® materials are alteration products of Mg-rich silicates. Three different types of contaminated water originating from different sources were prepared and analysed. These samples included (a) a multi-element solution prepared from trace element stock solutions; (b) rain water contaminated with motorway dust, and (c) contaminated water taken from an industrially polluted site (Cranleigh Brickworks, Surrey). Trace element analysis was undertaken by inductively coupled plasma mass spectrometry. Using a batch equilibrium procedure with optimised conditions of 0.25 g material in 50 ml solution for 5 min contact time, the mixing of the Blueguard® materials with a multi-element solution showed an effective removal of various trace elements under pH 4 to 9 conditions. These materials were then used to treat contaminated rainwater mixed with digested motorway dust. Trace element removal occurred from 80% for manganese up to 100% for lead. Analysis of surface water samples collected from the Cranleigh Brickworks showed that the levels of zinc and manganese were above the World Health Organisation (WHO) guidelines for drinking water. The most contaminated lagoon (25950 µg l⁻¹ Zn and 2843 µg l⁻¹ Mn) on the site was selected for laboratory and on-site testing of the Blueguard® materials. The best removal efficiency for these types of materials took place under a static design system where more than 95% of zinc and up to 97% of manganese was removed. Further investigation of the Blueguard® materials suggested the mechanism by which these materials reduce the level of trace elements in a solution was by precipitation, as a result of pH increase (through release of OH⁻(aq)). The results obtained for metal removal at Cranleigh has resulted in the application of these materials to remediate the site.
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<td>AES</td>
<td>atomic emission spectroscopy</td>
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<tr>
<td>BC</td>
<td>black carbon</td>
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<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
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<td>CRM</td>
<td>certified reference material</td>
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<tr>
<td>DDW</td>
<td>doubly deionised water</td>
</tr>
<tr>
<td>CSO</td>
<td>combined sewer overflow</td>
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<td>flame atomic absorption spectrometry</td>
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<td>United States Environmental Protection Agency</td>
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<tr>
<td>modif-UoS CPW</td>
<td>rain water from the car park mixed with digested motorway dust</td>
</tr>
<tr>
<td>VOC</td>
<td>volatile organic compounds</td>
</tr>
<tr>
<td>WHO</td>
<td>world health organisation</td>
</tr>
<tr>
<td>WWTP</td>
<td>wastewater treatment plants</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence spectroscopy</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>%</td>
<td>percentage</td>
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<tr>
<td>µ</td>
<td>micro</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
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<tr>
<td>L</td>
<td>litre</td>
</tr>
<tr>
<td>m</td>
<td>milli</td>
</tr>
<tr>
<td>M</td>
<td>molar</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>osc</td>
<td>oscillations</td>
</tr>
<tr>
<td>pH</td>
<td>the negative of the logarithm to the base 10 of hydrogen ion activity (-log$<em>{10}$[a$</em>{H^+}$])</td>
</tr>
</tbody>
</table>
## Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy of measurement</td>
<td>Closeness of the agreement between the result of a measurement and a true value, estimated by the mean of results</td>
</tr>
<tr>
<td>Adsorbate</td>
<td>The material adsorbed by the solid</td>
</tr>
<tr>
<td>Aeration</td>
<td>Process by which air is circulated through, mixed with or dissolved in a liquid or substance.</td>
</tr>
<tr>
<td>Aerobic</td>
<td>In the presence of air (oxygen)</td>
</tr>
<tr>
<td>Anaerobic</td>
<td>In the absence of air (oxygen)</td>
</tr>
<tr>
<td>Analyte</td>
<td>Material being analysed</td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>Effect resulting from human activity</td>
</tr>
<tr>
<td>Backscattering</td>
<td>Reflection of waves, particles, or signals back to the direction from which they came</td>
</tr>
<tr>
<td>Cathodoluminescence</td>
<td>Optical and electromagnetic phenomenon in which electrons impacting on a luminescent material</td>
</tr>
<tr>
<td>Diatomaceous earth</td>
<td>Soft and siliceous sedimentary rock</td>
</tr>
<tr>
<td>Hysteresis</td>
<td>Time-based dependence of a system's output on current and past inputs</td>
</tr>
<tr>
<td>Liquefaction</td>
<td>The transitions from solid and gas to liquid</td>
</tr>
<tr>
<td>Macroporous</td>
<td>Materials containing pore diameters of greater than 50 nm</td>
</tr>
<tr>
<td>Mesoporous</td>
<td>Materials containing pores diameters with diameters between 2 and 50 nm</td>
</tr>
<tr>
<td>Microporous</td>
<td>Materials containing pores diameters of less than 2 nm have</td>
</tr>
<tr>
<td>Nonpoint sources</td>
<td>Sources of pollution that originate from multiple sources over a relatively large area</td>
</tr>
<tr>
<td>Point sources</td>
<td>Pollution loads discharged at a specific location from pipes, outfalls conveyance methods from either municipal wastewater treatment plants or industrial waste treatment facilities</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Precision</td>
<td>The agreement of a set of replicate results among themselves, estimated by the standard deviation or relative standard deviation, rsd, reported as a %</td>
</tr>
<tr>
<td>Secondary electrons</td>
<td>Electrons generated as ionisation products</td>
</tr>
<tr>
<td>Softening</td>
<td>Removal of calcium, magnesium, and certain other metal cations in hard water</td>
</tr>
<tr>
<td>Solubility</td>
<td>The ability of a substance to go into solution (dissolve)</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>Surface area per unit mass</td>
</tr>
<tr>
<td>Substrates</td>
<td>Materials used to construct wetlands include soil, sand, gravel, rock, and organic materials such as compost</td>
</tr>
<tr>
<td>Surge</td>
<td>Sudden changes in the flow rate</td>
</tr>
</tbody>
</table>
Acknowledgements

I would like to thank my main supervisor Prof Neil Ward who I believe is proof that a perfect supervisor exists. No words can express how grateful I am for his constant support and genuine engagement during my PhD journey. Conducting a PhD in the Chemistry department, considering my engineering background, would be impossible without his valuable patience and passion for me to succeed.

A special thank you to my other main supervisor Prof Robert Slade, I truly appreciate his advice and easy approachableness as a supervisor. He has devoted much of his time imparting to me his valuable technical knowledge and guidance as well as supporting me with securing funding for my project.

I would also like to thank:

Dr Justin Hamilton for his continuous encouragement and insightful comments. Without his support it would not be possible for me to conduct this research.

Sibelco Ltd for generously supplying me with the material used in this research, as well as the financial contribution for my bench fees, and also for their advice, data and analyses where required.

My colleague and best friend Wafa Al-Rawahi who has been very generous in helping me experimentally and having useful technical discussions.

The Grundy Trust for assisting me with my educational maintenance during my research.

Richard Armfield of the Cranleigh Brickworks, Surrey who provided access to the site and gave support and directions during the sampling trips.

I would also like to thank the following people, in alphabetical order, for experimental support and technical advice: Dr Alex Roberts, Dr Ana Markowska, Anamika Sharivastava, Dr Andrea Petronda, Dr Cathryn Hancock, Dr Daniel Driscoll, Fernanda Vanoni Matta, Dr Gillian Lord, Hazim F EL-Sharif, Hibbaq Mohamud, Judith Peters, Dr Kevin Young, Maisarah Jaafar, Dr Sami Al-Aibi and Dr Simon Poynton.
Chapter 1 Literature Survey

1.1 Introduction
This chapter provides an introduction to different types of water and wastewater pollution. Both sources of pollution entering the environment including point source (PS) and non-point source (NPS) are then discussed with particular emphasis on stormwater contamination (a non-point source) as a result of motorway pollution; and an industrial discharge contamination (a point source) relating to chemical contamination of water. The characteristics and chemistry of each source are reviewed with a stress on trace elements as a specific type of chemical released via water systems into the environment. Measures and technologies for wastewater treatment processes from an engineering point of view, as a main consideration of this study, are also debated.

1.2 Sources of Water and Wastewater Pollution
Human activities by deteriorating the quality of rainwater as well as discharging waste to the environment can pollute water bodies and contaminate natural systems. These activities, such as the inappropriate disposal of urban and industrial effluents or non-selective applications of agrochemicals, are some of the main factors influencing water quality (Azizullah et al., 2011). Disastrous incidents, such dam bursts as a result of inadequate management (www.1), are another example of adding to the serious levels of contamination and toxicity of water bodies. Any physical, chemical or biological factors which cause harmful effects on aquatic life and water consumers can contribute to water pollution (Goel, 2011).

In General, water is extracted from four main sources which play an important role in water chemistry and, subsequently, the application of a method of water treatment. These sources include:

- groundwater which may be safe in terms of bacteriology and might require treatment, such as aeration and softening;
- rivers which, depending on the point of water abstraction, may need considerable treatment;
• natural lakes which might require different levels of treatment based on factors such as trophic condition and the presence of sewage treatment works;
• man-made lakes and reservoirs (similar to lakes but with better management and thus different degrees of treatment) (Scholz, 2006).

Wastewater originates predominantly from water usage by residences, commercial and industrial establishments and will influence the quality of ground and surface waters (Figure 1-1). Physical, chemical, and biological characteristics of wastewater are criteria which define the quality and thus type of required treatment (Henze, 2002). The Environment Agency’s (UK) wide range of statutory responsibilities, covers regulation, management of the environment and to administer, monitor and reinforce regulations. The areas of responsibility include: pollution by industry, regulation of disposal of radioactive waste and controlled waste, regulation of the remediation of contaminated land (www.2). The four main sources of wastewater are: (1) domestic sewage, (2) industrial wastewaters, (3) agricultural run-off, and (4) storm water and urban run-off (Ramalho, 2012).

![Figure 1-1 Sources of wastewater (Tchobanoglous & Burton, 1991)](image)

Pollutants which enter the water environment are classified into two main categories: non-point source (NPS) and point source (PS) (EPA, 2012). Non-point source pollution originates from diffuse sources moving over and through a
large area (Tchobanoglous & Burton, 1991). This type of pollution begins as rainfall or snowmelt and, whilst in transit as run-off, picks up and carries away natural and human-made pollutants. Ultimately, this water ends up in lakes, rivers, wetlands, coastal and ground waters (www.3). Point source (PS) pollution, on the other hand, is discharged at a specific location from either municipal or industrial wastewater treatment facilities (Tchobanoglous et al., 1991). Therefore, the resultant wastewater can vary significantly in terms of physical, chemical and biological composition and the level of contaminants (Gutterres & de Aquim, 2012).

Motorway and dual-carriageway surfaces in developed urban areas are one of the major non-point sources of pollution which accumulate a variety of chemicals, such as, suspended solids, anions and cations, trace elements, polycyclic aromatic hydrocarbons (PAHs) and de-icing salts (Kayhanian 2012; Duong & Lee, 2011; Christoforidis & Stamatis, 2009; Aryal et al., 2005; Mungur et al., 1995). Vehicular traffic also a source of various emissions including nitrogen oxides (NO\textsubscript{X}), volatile organic compounds (VOC), carbon monoxide (CO), carbon dioxide (CO\textsubscript{2}) and particulate matter (PM), mostly in the form of black carbon (BC) and organic carbon (OC) (Sawyer et al., 2000). Emission control regulation has been very successful in reducing exhaust emission pollution. However, the levels of non-exhaust emissions from road vehicles are not reducing in UK transport (Thorpe & Harrison, 2008).

Non-exhaust pollution, such as, brake, road and tyre wear, and road dust contribute to motorway pollution in addition to exhaust pollution (Thorpe & Harrison, 2008). This type of traffic has been identified as the main source of Pb, Cu, Cd, and Zn by Legret and Pagotto (1999). They also have reported that brake linings, tyre rubber and de-icing salt contain Pb, Cu, Cd and Zn. It should be noted that lead levels should not now be a major problem since the introduction of non-leaded fuels in the late 1990s. Hjortenkrans et al. (2007) found that Cu and Zn emissions from brake linings were unchanged in 2005 compared to 1998. They also showed that tyres are the main source of Zn and Cd emissions in Stockholm, Sweden. Road dust (RD) can be considered as a monitor of emission of traffic-related metals from motorways (Świetlik, et al., 2015). Heavy metals released into the environment through RD particles have been discussed in over
300 articles and the most recognised and examined ones are Cd, Cr, Cu, Ni, Pb and Zn (Werkenthin et al., 2015).

Urban improvement leads to an increase in impervious areas (roads, driveways and buildings) and consequently an increase in stormwater run-off (refer to Figure 1-2, Grant et al., 2003). Urban stormwater is rainfall and snowmelt that runs off the land and enters streams, lakes and storm-sewers (Ministry of the Environment, 2003). During rain events and snowmelt, stormwater transports motorway pollutants into the storm drainage system, from where they either reach treatment facilities or are directly discharged to receiving waters. Stormwater runoff contains a large variety of chemical contaminants e.g. trace elements (Pb, Zn, Cu, Cd, Cr and Ni), organic compounds, nutrients, solids, anions and cations, suspended solids and de-icing agents (Legret & Pagotto, 2006; Grant et al., 2003; Barbosa & Hvittved-Jacobsen 1999). The United States Environmental Protection Agency reported on this topic (USEPA, 1995). Trace elements can be toxic and ubiquitous, and they cannot be chemically transformed or destroyed. They are therefore of particular importance in stormwater runoff (Davis et al., 2001). Dissolved copper in motorway stormwater, for example, exceeds the USEPA criteria (9.0 µg l⁻¹) in approximately 75% of the samples (Camponelli et al., 2010). Therefore, in order to maintain the health of streams, lakes and aquatic life, stormwater should be managed and if possible, the load of chemical contaminants reduced before discharge into watercourses.

Figure 1-2 Stormwater contaminants (Grant et al., 2003)
Water contaminants are categorised in three groups, including:

(1) physical contaminants such as thermal pollution, colour, turbidity, foams and radio activities and insoluble contents (Ramalho, 2012 and Henze, 2002);

(2) chemical contaminants, including both organic and inorganic contaminants.

Organic contaminants are mainly of concern due to oxygen depletion as a result of the utilisation of dissolved oxygen during the biodegradation of organic compounds (Ramalho, 2012). There are thousands of different organics in wastewater and individual measurement of each organic compound is impossible. Therefore, various collective analyses, based on an equation of oxidation reaction of organic matter (OM), are used. The consumed amount of oxygen or the produced amount of carbon dioxide (as a result of oxidation of organic matter) can be measured using different methods (Henze, 2002). These measurements, which are in association with the organic content, include biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and total oxygen demand (TOD) (United Nations, 2003). Inorganic contaminants are also a pollution of concern as they can be toxic. Parameters related to inorganic contaminants include salinity (dissolved salt content), hardness, pH, acidity and alkalinity, as well as levels of ionised metals, and anionic entities such as chlorides, sulfates, sulfides, nitrates and phosphates (Henze, 2002); and

(3) biological contaminants are organisms in the water which can transmit diseases like cholera, typhoid and paratyphoid (Ramalho, 2012). Measuring parameters related to biological contaminants include coliforms, faecal coliforms, specific pathogens and viruses (Henze, 2002).

Metals are not biodegradable and can therefore, unlike most organic pollutants, accumulate in living tissues (Barrera-Díaz et al., 2012). Industrial discharge from various commercial activities, along with stormwater can contain heavy metals that pose a possible health risk to animals and humans. The term “heavy metals” has often been applied to elements with densities above 5 g cm\(^{-3}\). The term “trace metals” are used for metals, such as zinc, which are necessary in trace amounts for organisms to grow, but they can be toxic in excess quantities (Fürstner & Wittmann, 2012). Despite the necessity of some heavy metals as nutrients for
plants metabolism, excess levels of such metals in waste streams, groundwater and soils are extremely toxic and can cause serious damage to the receiving micro and macro environment (Sharma & Sanghi 2012). Nowadays, heavy metals are environmental priority pollutants, being known to be toxic or carcinogenic, and are therefore the subject of more and more strict regulations. The common heavy metals present in wastewater include cadmium, chromium, copper, iron, lead, nickel, and zinc. All can cause risks to animal and human health (Jaishankar et al., 2014).

1.2.1 Aluminium

Aluminium is the most abundant (8.3% by mass) metallic element and the third most abundant of all elements (after oxygen and silicon) (Greenwood and Earnshaw 1997). There is evidence that it is associated with breast cancer; where it can increase migration and invasion of human breast cancer cells (Darbre 2016). Aluminium’s free metal cation, in the form of Al\(^{+3}\), is highly biologically reactive and available despite being non-essential (Exley 2016).

While natural processes are the main cause of aluminium being released to the environment, several factors influence mobility of this element and subsequent transport within the environment. These include chemical speciation, hydrological flow paths, soil–water interactions, and the composition of the underlying geological materials (WHO 1997). The maximum allowed level of aluminium in drinking water by the EPA (2012) and UK Statutory Instruments (UKSI) (2016) is reported as 0.2 mg l\(^{-1}\).

1.2.2 Cadmium

Cadmium (Cd), without being essential for living organisms, is known as one of the most toxic heavy metals. Cadmium may be released into the environment as a result of human activities, such as, the production of nickel cadmium batteries, cell phones, and photovoltaic cells of solar panels, metal smelting, synthetic pigment production, metal coatings, run-off from waste batteries, rainwater run-off from a mining area and the incineration of solid wastes are the main anthropogenic sources of cadmium (Patar et al., 2016; Purkayastha, 2014). Cadmium can cause serious health effects, such as, kidney damage, renal disorder and is a human carcinogen (Barakat, 2011). Findings by Patar et al.,
2016, showed that the presence of cadmium in the aquatic environment can significantly damage DNA in amphibians. The maximum contaminated level for this element allowed by WHO (1998), EPA (2012) and UKSI (2016) for drinking water is reported as 0.005 mg l\(^{-1}\).

### 1.2.3 Chromium

Chromium (Cr) has in recent years been of major concern because in the environment it can be present in various oxidation states ranging from -2 to +6 valences. The most important oxidation states of chromium are 0 (element metal), +3 (considered to be a trace element essential for living organisms to function properly) and +6 (considered to be toxic in relation to biological systems) (Dirilgen & Doğan, 2002). Hexavalent chromium is toxic and can damage genetic material, usually DNA, and is a potential carcinogen (Zhou et al., 2016; Altundogan, 2005). It is released into the environment as a result of effluent from industries including dying, fertiliser manufacture, electroplating, leather tanning, cement, mining, and photography; ranging from 0.5 to 270 mg l\(^{-1}\) (Sharma & Sanghi, 2012). The maximum allowed level of chromium in drinking water by the WHO (1998), EPA (2012) and UKSI (2016) is reported as 0.005 mg l\(^{-1}\).

### 1.2.4 Copper

The dissolution of minerals in natural water results in the release of copper (Cu) within the range between 1 and 10 µg l\(^{-1}\). The main sources of copper produced by anthropogenic activities are from agriculture and industrial effluent discharge from the manufacturing and refining of copper, steel production, electrical components and electroplating (Odobasic, 2012). Copper is not readily bio-accumulated and thus its toxicity to human beings and other mammals is relatively low compare to other heavy metals. However, this element disturbs the metabolism and decreases the enzymes of some plant if the level of copper in the tissue is slightly higher than the required level (Fernandes and Henriques 1991). From a toxic point of view, Cu\(^{2+}\) can deposit in the brain, skin, liver, pancreas and myocardium (Sharma & Sanghi 2012). Copper plays an important role in animal’s metabolisms; the excessive ingestion of copper, however, brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death (Paulino et al., 2006). The maximum permitted level of copper set in the
guidelines of the WHO (1998), EPA (2012) and UKSI (2016) for drinking water is reported as 2, 1 and 2 mg l\(^{-1}\), respectively.

### 1.2.5 Iron

Iron (Fe) is the second most abundant metal and the fourth most abundant element in the Earth’s crust. It can vary in terms of chemical speciation, concentration and bioavailability in natural waters depending on the type of receiving wastewater (Xing & Liu 2011; Pehkonen, 1995). This element exists in a variety of rock and soil minerals both as Fe\(^{2+}\) and Fe\(^{3+}\) (Pehkonen 1995). Although iron is biologically of great importance for most living creatures, it can damage biomolecules, cells, tissues and the whole organism and increase the risk of lung cancer (Jaishankar et al., 2014; Nelson, 1992). Iron and the related Fe-compounds have been known to be released into the environment in large quantities as a result of industrial activities. Industries connected with the production of constructional materials for drinking-water pipes, food colours, coagulants (in water treatment), pigments in paints and plastics are the main sources of iron in effluent (Tautkus et al., 2004). The maximum permitted level of iron in drinking water as set by the guidelines of the WHO (2004) and UKSI (2016) is reported as 0.3 and 0.2 mg l\(^{-1}\), respectively.

### 1.2.6 Lead

Lead (Pb) is a non-essential and very toxic metal which has a very deleterious effect on biological systems (Pattee & Pain, 2003). Lead can cause serous physiological and neurological effects on humans, including irreversible brain damage, kidney diseases, cardiovascular effects and reproductive toxicity (Sharma & Sanghi, 2012; Lanphear et al., 2005). Industrial activities, such as, mining and smelting, battery production as well as the combustion of fossil fuels (including coal, gasoline) results in high levels of lead in wastewater (Komárek et al., 2008 and Ahlberg et al., 2006). The maximum permitted level of lead in drinking water set in the guidelines by the WHO (1998), EPA (2012) and UKSI (2016) is 10, 15 and 10 µg l\(^{-1}\), respectively.
1.2.7 Manganese

Manganese (Mn) can be found in natural waters in two oxidation states: Mn(II) and Mn(VII) (Roccaro et al., 2007). Manganese is present in industrial discharge as a result of its application in ceramics, dry battery cells and electrical coils (Shafaei et al., 2010). This element at excessive levels can cause neurological disorders, including psychotic behaviour, and criminality, (Al-Zoubi, at al., 2015). The maximum permitted level of manganese drinking water set in the guidelines by the WHO (1998), EPA (2012) and UKSI (2016) is 400, 50 and 50 µg l$^{-1}$, respectively.

1.2.8 Nickel

Industries including electroplating, electronics, and metal cleaning often discharge high levels of nickel or Ni(II) ions (Akhtar et al., 2004). Nickel is known to be a carcinogen, with excessive levels of nickel reported to cause serious lung and kidney problems, (Fu & Wang, 2011; Borba et al., 2006). The maximum permitted level of nickel in drinking water set in the guidelines by the WHO (1998), EPA (2012) and UKSI (2016) is 20, 15 and 20 µg l$^{-1}$, respectively.

1.2.9 Zinc

Zinc (Zn) is an essential metal which is required in small doses for metabolic and physiological functions of living organisms and is involved in the regulation of oxygen transport, as well as many other important biochemical processes. However, too much zinc can produce deleterious effects and cause health problems, such as stomach cramp, skin irritation, vomiting, nausea and anaemia (Oyaro et al., 2007). Zinc has been reported to bioaccumulate in fish (Odobasic, 2012). Industrial activities, such as paint manufacturing, textile dyeing, mining, coal and waste combustion, steel works and pigment manufacturing results in high levels of zinc in wastewater (Al-Zoubi, at al., 2015; Cristian et al., 2015). The maximum permitted level of zinc in drinking water set in the guidelines by the EPA (2012) is 5000 µg l$^{-1}$.

1.3 Wastewater Treatment Technologies

As mentioned before, the contamination of fresh water is growing as a result of the discharge of various industrial and natural chemical compounds into water
systems. As a result of the diversity of these contaminants different wastewater treatment technologies have been developed and applied (Schwarzenbach et al., 2006). Globally, several investigations have been carried out to study industrial effluent influencing the ecology of receiving water bodies; as well as suitable treatment technologies based on a laboratory optimization and industrial pre-scale trials (Prieto, 2015 and Sun, 2016). However here is not much evidence of this type of research being carried out in the UK, recently.

1.3.1 Stormwater treatment facilities

Considerable proportions of chemical pollutants are dissolved in stormwater and many others are attached to fine particles of silt, which do not easily settle. Removing these contaminants needs a complex combination of processes such as sedimentation, adsorption, and filtration (TP10, 2003). Stormwater treatment facilities (STFs) are required to reduce or remove chemical contaminants from runoff. These facilities are eco-technological facilities that employ natural processes to remediate stormwater pollution (Larm, 2000). Stormwater management ponds are designed to hold runoff from impervious surfaces and allow the settling of sediments and associated pollutants. They are a controlled environment, which employs the natural processes involving wetland vegetation, soils, and their associated microbial assemblages to treat wastewater (Hammer & Bastian, 1989).

Stormwater treatment facilities (STFs) are engineered measures implemented to control flow rate, flooding and to remove physical and chemical contaminants. They include wet and dry ponds (retention and detention ponds), constructed wetlands, open ditches and green structures such as grassed swales, infiltration trenches and infiltration strips.

Detention and retention basins

Detention and retention basins were originally designed as flood control reservoirs but more recently they have an additional role, which is in water quality control and environmental protection. For the purpose of easier communication, a terminological distinction is made between “detention basins” and “retention basins” (in the literature, the term “basins” is often substituted by “ponds”, implying small urban facilities).
Detention basins (dry ponds) are, by definition, facilities which temporarily store stormwater run-off to control the peak rate of discharge and provide water quality treatment, primarily through the incorporation of extended detention. They then release water at a slower rate than is collected by the drainage system, with very little infiltration of the stored stormwater. These ponds are normally dry between storm events, thus they act as “dry” basins (TP10, 2003).

Retention basins (wet ponds) are permanent “wet” basins, which have a standing pool of water. These ponds are a part of the drainage system designed to control flood flows during storm events, and to provide water quality treatment. Retention basins in most cases have better removal rates for solids than temporary detention basins, due to the fact that retention basins are permanent storage facilities, allowing further water treatment in time intervals between storms. A retention pond is a part of a drainage system designed to control water flow during rainstorms and to trap contaminated solid particles washed off by runoff water from a motorway.

**Constructed wetlands**

Constructed wetlands are built to slow down runoff movement to streams as well as to store pollutants. They are low cost and low maintenance systems which are being used for removing pollutants (Lim et al., 2003). Wetland ecosystems generally can be defined by the presence of saturated soils and plants that grow well under these conditions and assist the treatment process by reducing velocities and biological uptake (TP10, 2003).

Hydraulic short-circuiting is one of the issues that needs to be addressed, when it comes to constructing wetland plants as facilities to improve water quality. Constructed wetlands should mimic the natural system, therefore, it’s important to scale up the experimental design of the wetland facilities to simulate this natural system (Mitchell et al., 1995).

The dynamic nature and the seasonal conditions should be taken account when the laboratory data are applied on a field scale for storm water pond system (Bartlett et al., 2012).
1.3.2 Industrial wastewater treatment

There is a growing requirement to treat industrial wastewater as a result of factors including water shortage, massive wastewater discharge from various industries, and increasingly strict wastewater discharge standards (Zheng et al., 2015). Industries, depending on the process, may require large volumes of water for different purposes including cooling (power plants, steel mills, and distillation industries), processing (breweries, pulp and paper mills), cleaning (textile mills, abattoirs), transporting products (beet and sugar mills) and flushing wastes (Gutterres & de Aquim, 2012).

Metals are present in industrial wastewater as a result of either their direct application in various industrial processes or their presence in chemical reagents and/or related materials commonly used in the various industrial activities resulting in the production of the effluent (Euvaard, 2014). These metals, afterwards, make their way to water bodies, either by direct discharge or indirectly passing first by a municipal wastewater treatment plant.

As shown in Figure 1-3 and Figure 1-4, wastewater treatment levels are known as pre-treatment, primary treatment, secondary treatment followed by tertiary treatment (the latter being advanced treatment). Primary treatment involves separating a portion of the grit and suspended solids from the wastewater before it is discharged to a municipal wastewater treatment plant.

Physical mechanisms from which contaminants are removed at the primary treatment stage include:

(1) screens which remove debris to avoid the clog of the machinery;
(2) chambers into which wastewater flows (where heavy solids such as sand and grit sink to the bottom);
(3) primary settling tank where a significant portion of the organic solids settles to the bottom while fats, oils and grease rise to the top; and
(4) revolving ‘arms’ which simultaneously scrape the primary (untreated) solids from the bottom and skim the grease from the top (Krantzberg et al., 2010).
Secondary treatment involves aerobic biological processes to remove dissolved organic matter from wastewater. Sewage micro-organisms are cultivated and added to the wastewater. These microorganisms absorb organic matter from the wastewater as a supply (Krantzberg et al., 2010).

Tertiary treatment is a final stage to improve the effluent quality before it is discharged to watercourses and land. There might be more than one tertiary treatment process used at any treatment plant. Disinfection (effluent polishing) might also be carried out as the final process. Tertiary treatment may include:

1. filtration such as sand filtration (which removes much of the residual suspended matter) and filtration through activated carbon (which removes residual toxins);
2. removal of nutrients such as nitrogen and phosphorus using biological processes, chemical precipitation or filters;
3. disinfection to destroy bacteria which can cause disease in humans (Krantzberg et al., 2010).

As mentioned earlier, wastewater treatment methods are broadly classifiable into physical, chemical and biological processes.
1.3.3 Physical unit operation

Physical unit operations are one of the first treatment methods used and are the basis of most process flow systems. This method applies physical forces to remove contaminants from the solution. The most commonly used physical unit operations include: screening, comminution, flow equalisation, sedimentation, flotation and granular-medium filtration.

**Screening**

Screening is the first unit operation used at wastewater treatment plants (WWTPs). This method removes objects such as rags, paper, plastics and metals to prevent damage and clogging of downstream equipment, piping and appurtenances. There are two types of screens: coarse screens (Figure 1-5), designed to remove large solids, rags, and debris with typical openings of 10 mm or larger; fine coarse screens designed particularly in systems that lack primary treatment. Fine screens have opening sizes of about 3 to 10 mm and are used to remove materials that may cause operation and maintenance issues in downstream processes (Nozaic & Freese, 2009).

![Image of a typical coarse screen](image-url)

**Figure 1-5 Typical coarse screen (Nozaic & Freese, 2009)**
**Comminution**

The “comminution” itself includes all terms associated with the size reduction such as crushing, cutting, grinding and milling. One of the purposes of this method is to reduce the size of raw materials to the desired size for subsequent processing (Gupta, 2006). This technique is mostly applied when screening treatment is impractical (United Nations, 2003).

**Flow equalisation**

Flow equalisation is a process of controlling flow rate and hydraulic velocity in order to minimise the variability of water and wastewater flow rates and composition (Goel, 2005).

Flow equalisation is of importance as the existence of wide variations in flow composition over time may degrade the process performance and efficiency of a treatment system (Akpor et al., 2014). Khan et al., (2006) summarised the purpose of equalisation for industrial treatment facilities as follows:

1. flow surge minimisation to the treatment systems and match rate of chemical feed with that of feeding equipment;
2. adequate pH control;
3. reducing chemical requirements necessary for neutralization;
4. providing continuous feed to biological systems over periods when the manufacturing plant is not operating; and
5. preventing entry of high concentrations of toxic materials to biological treatment plant.

Equalisation practice can be located in-line or off-line in the treatment system. For in-line equalization, the whole incoming raw wastewater directly enters into the basin, which is then pumped directly to other treatment units, such as primary treatment units. However, for off-line equalisation an overflow structure diverts excess flow from the incoming wastewater into the basin from where it is pumped into the treatment stream (Figure 1-6).
Sedimentation

Sedimentation is the separation of suspended particles from water by density difference between the solid particles and the bulk of liquid. Two main groups of sedimentation are gravity and centrifugal settling. Gravity sedimentation takes place under the effect of gravity and flocculation agents are often used to improve the settling (André, 2015). The most common coagulants in use include aluminium sulfate, ferric sulfate, ferric chloride and poly-aluminium chloride. These coagulants, when mixed with water, form hydroxide precipitates which are fluffy and enmesh particles, microbes and dissolved organic carbons (WHO, 2003).

Flotation

Flotation is a water treatment process from which suspended solids are removed from wastewater by generating gas bubbles in the wastewater. In this process the released air attaches to suspend particles and causes the apparent density of bubble-solid agglomerates to be less than that of water; agglomerates therefore float to the surface (Zable, 1992). The main applications of flotation in wastewater treatment have been in the removal of the solids, ions, macromolecules, fibres, and other materials from water (Rubio, 2002). There are different types of flotation process based on the method by which the gas bubbles are produced (Zable, 1992).

Filtration

Filtration is a process in which the solid liquid mixture is directed towards a medium (filters) such as screen, paper, woven cloth, membrane, etc (Rushton, 2008). In this process, water passes through the beds of granular materials so as
to improve clarity and remove microorganisms (Betancourt, 2004). Filtration through sand and gravel has been a method of clarifying and purifying water for thousands of years (Crittenden et al., 2012). Bed materials can be made of a variety of components including: (i) a bed of sand (sand filtration) or (ii) a layer of diatomaceous earth (diatomaceous earth filtration), or (iii) a combination of coarse anthracite coal overlying finer sand (dual- and tri-media filtration) (Betancourt, 2004). Filters used in water treatment are also categorised on the basis of: (i) driving force (gravity filters and pressure filters), (ii) direction of flow (up and down flow filters), and (iii) filtration rate (slow sand filter and rapid sand filters) (Al-Aibi, 2011).

1.3.4 Chemical Unit Operation

Chemical processes which induce chemical reactions, are called chemical unit processes. There are several distinct chemical unit processes, including chemical precipitation, ion exchange and adsorption processes (Fu & Wang, 2011).

1.3.5 Precipitation

The formation of solid particles from dissolved materials in water, above a specific solubility limit, is called precipitation. The conceptual mechanism of trace element removal by chemical precipitation has been presented by Wang et al. (2004). In this method the pH of the solution is manipulated by adding alkaline agents. The solubility of the heavy metal is reduced and the ion is precipitated in the form of a hydroxide. The conceptual mechanism of heavy metal removal by hydroxide precipitation is presented in Equation 1.

\[ M^{2+} + 2(OH^-) \rightleftharpoons M(OH)_2 \downarrow \quad \text{Equation 1} \]

\( M^{2+} \) and \( OH^- \) are the dissolved metal ion and the precipitant, respectively, while \( M(OH)_2 \) is the insoluble metal hydroxide. Adjustment of pH to values between 9 and 11 may significantly improve heavy metal removal by chemical precipitation (Shim et al., 2014).

This method has, however, some disadvantages such as: cost and type of the precipitating agent and the volume of the resultant insoluble compounds produced. Moreover, the presence of some ions, such as cyanide and
ammonium, may produce complexes with metal ions, which are then difficult to precipitate.

Trace element removal through precipitation is affected by pH (an increase in pH causes an increase in the percentage of trace elements removal). Therefore, the pH of the solution should be determined when a solid material is added to the solution (Nagwan et al., 2007). The formations of precipitates are chemical equilibrium phenomena, and known as the equilibrium constants solubility products, Ksp. These values are derived from the concentrations of ions in equilibrium reactions; the higher the concentrations of ions, the greater the Ksp (Lide, 2007).

Various factors including temperature, ionic strength, and complex formation of other solids, alkalinity and buffers can directly affect the solubility of metal hydroxide. The change in ambient conditions and wastewater temperature do not considerably affect the precipitation performance (Wang and Hung, 2004).

Controlled pH and temperature, as well as an appropriate concentration of the undesirable ion, are necessary for successful precipitation. Chemical precipitation is ineffective when levels of metal ions in solution are below 100 mg l\(^{-1}\) (Cechinel, et al., 2016; Kumar et al., 2015; Nourbakhsh et al., 1994). Research carried out by (González-Muñoz et al., 2006) showed that precipitation using sulfide can be successful in reducing the metal content and by combining this method with nanofiltration, the solution is capable of being directly reused. During precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. Sedimentation or filtration process can be used afterwards to separate the insoluble precipitates from water before appropriately discharged or reuse (Purkayastha et al., 2014; Fu & Wang, 2011).

### 1.3.6 Ion exchange process

Ion exchange is a simple method in which unwanted ions from solution are transferred to solid materials which do not pollute the environment (Dąbrowski et al., 2004). Solid phase materials, in return, give back an equal amount of harmless ions to the solution. The most common cations in solid materials, which are used to exchange cations with the metals in the waste streams, are Na\(^+\), Ca\(^{2+}\) and K\(^+\) (Inglezakis et al., 2005). High treatment capacity, high removal efficiency
and fast kinetics are the benefits of using the ion exchange method with natural and synthetic resins (Fu & Wang 2011).

Ion exchange of the trace element is dependent on the initial concentrations of the adsorbent, sorbate, time of contact and pH level (Gode & Pehlivan, 2006). Abo-Farha et al. (2009) showed that charge density and hydrated ion diameter play an important role in the trace element removal process using cation exchange resins.

Tetravalent metal acid (TMA) salts have emerged as promising advanced materials, as they possess robust properties, such as ion exchange characteristics, thermal stability and chemical resistivity. TMA salts have the general formula:

\[ M(IV)(HXO_4)_2 \cdot nH_2O \quad \text{Formula 1} \]

Where \( M \) = Zr, Ti, Ce, Th, Sn, etc. and \( X \) = P, Mo, W, As, Sb, etc. (Jayswal & Chudasama, 2007; Maheria & Chudasama, 2007). These materials are considered as inorganic ion exchangers, since the protons of the constituent OH group of the anion can be exchanged for several metal ions.

Anbia and Ghassemian (2011) showed that mesoporous silicate materials, containing zirconium and iron ions can be used as absorbents for cadmium and copper removal from the solution.

The efficiency of ion exchange of porous materials can be reduced, due to surface precipitation and the blockage of the micropores by a precipitated phase. (Misaelides et al., 1995). Inglezakis et al. (2005) showed that the presence of other cations in water decreases the trace element uptake due to the simultaneous exchange of positively charged cations which competitively occupy available exchange sites in the ion exchange materials.

### 1.3.7 Adsorption process

The process by which a substance accumulates at the interface between two phases, such as solid and liquid or solid and gas, is called adsorption. The adsorbed substance at the interface is termed the ‘adsorbate’ and the solid on which adsorption happens is the ‘adsorbent’ (Bhatnagar & Sillanpää, 2010).
Barakat (2011) divides pollutant sorption onto a solid phase into three steps: (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle (if that occurs).

Adsorption, while being one of the most effective methods for the removal of trace elements, can be problematic when it comes to filtration, centrifugation or gravitational separation of adsorbent from the aqueous solutions (Lingamdinne et al., 2015).

1.3.8 Forward Osmosis (FO) and Reverse Osmosis (RO) Processes

Osmosis is the net movement of liquid through a selectively permeable membrane as a result of difference in osmotic pressure. A selectively permeable membrane rejects solute molecules or ions while allowing passage of water (Cath et al., 2006). This physical phenomenon has application in separation processes for wastewater treatment, food processing, and seawater/brackish water desalination. The principle of forward osmosis (FO) process relies on using the natural osmotic process to draw the water molecules across a semi-permeable membrane from saline feed water to a higher concentration solution, namely the draw solution. In fact, FO does not require a high applied hydraulic pressure and thereby membrane base technology has not only the potential to reduce both capital and operation cost but can also be beneficial for fouling control compared to pressure-driven membrane processes (Phillip et al., 2010). The reverse osmosis (RO) phenomenon takes place by reversing the FO process and making the solvent filter out of high concentration into lower concentration solution and is illustrated in Figure 1-7. FO uses the osmotic pressure differential (\(\Delta\pi\)) across the membrane, while in a RO hydraulic pressure differential (\(P\)) is applied, as the driving force for transport of water through the membrane. For RO, water diffuses to the less saline side due to hydraulic pressure (\(P > \pi\)) (Cath et al., 2006).
1.4 Solid Phase Materials for Chemical Removal of Wastewater contaminants

1.4.1 Zeolites

There are many reports on the application of zeolites in removing trace elements from water (Doula, 2009; Erdem et al., 2004). By mixing a zeolite by-product and other materials, researchers have been able to produce cheaper alternatives for the treatment of metal contaminated wastewater (Ok et al., 2007).

There are two approaches to the kinetics of the ion exchange of zeolites. One is an assumption based on diffusion of exchangeable ions through the channel / void system of zeolites and the other approach assumes the zeolite as an open structure with all its cations being simultaneously available for exchange with the cations from solution (Biškup & Subotić 2004).

Mihaly Cozmuta et al., (2012) summarised the most important parameters that influence the adsorption of cations on zeolites, as follows:

1. the concentration of metal ions in solution;
2. the ratio between the volume of solution and the mass of zeolite (the ratio between solid and liquid),
3. the pH of the contact solution,
4. the initial parameters of the zeolite i.e. physico-chemical treatment and the type and concentration of activating solutions used,
5. temperature,
6. the average diameter of the particle,
(7) the nature of the anion accompanying the cations, and
(8) the hydrated radii of adsorbed ions and the magnitude of the dehydration energy.

1.4.2 Activated carbon

The efficiency of granular activated carbon (GAC) in removing trace elements through adsorption has been examined by Jusoh et al., (2007). They showed that GAC can successfully remove cadmium and lead through a column test. In order to use activated carbon as an absorbent to remove organic and inorganic pollutants from the aqueous phase, the activated carbon should be modified. Rivera-Utrilla et al. (2011) have categorised the methodologies of modification into four groups: oxidation, sulphuration, ammonification and coordinated ligand anchorage.

Modification and characterisation of activated carbon in order to enhance its adsorption efficiency is one of the novel and attractive topics in the water treatment area (Streat et al., 2004). The surface functional group and high surface area play an important role in the efficiency of activated carbon as an adsorbent (Melegy, 2010). The large adsorptive capacities of activated carbon are closely connected with the pore structure via specific surface area (SSA), pore volume and pore size distribution (Cao et al., 2006). Nearly all inexpensive carbonaceous materials can be considered as starting materials for the production of activated carbon (Muñoz-Guillena et al., 1992).

1.4.3 Lignite

Lignite contains carboxyl and hydroxyl groups which make it a very active material for ion exchange processes. Jochová et al. (2004) showed that calcium-loaded lignite can be used as an inexpensive ion exchange material for trace element removal. The selectivity of the sorbent decreases by the sequence: Pb > Cr³⁺ > Fe²⁺ > Cu > Zn ≥ Cd ≥ Co ≥ Ni.

1.4.4 Olivine

The natural mineral olivine is composed of silicate tetrahedra, and iron and magnesium, (Mg, Fe)₂ SiO₄. The Fe and Mg content can vary marginally, depending on the geological origin (Koppatz et al., 2011). In many natural
crystals, and particularly in the more iron rich members of the series, some of the Mg or Fe is replaced by other elements, such as Mn and Ca. At the magnesium rich end of the series, Cr and Ni (generally in small amounts) are usually present (Deer et al., 1997). In spite of its simple chemical composition, olivine may also contain a number of significant minor elements, such as Ti, Al, Mn, Ca, Cr, Ni and Co in low concentrations, most of which are below 0.1 mass% of oxide, with the exception of NiO (Sobolev et al., 2009).

Trace elements in olivine can be divided into three categories, namely;

(1) Category I elements (Ni, Mn, Co, Cu, Zn, and Li) show a narrow range of concentrations and olivine is the major host mineral. The group are mostly divalent elements with ionic radii close to that of Mg and often show correlations with the Fe content;

(2) Category II elements (Cr, Al, V, Sc, Ca, and Na) show a large range of concentrations, controlled mainly by the equilibration temperature of the rock. These elements fit less comfortably into the olivine lattice than Category I elements because of the charge or size, and are strongly concentrated in co-existing mantle minerals.

(3) Category III elements (Ti, Zr, Nb, Y, and P) show the largest range of concentrations in olivine, which are mostly controlled by the bulk rock content. They are strongly incompatible in olivine as well as co-existing in rock-forming mantle minerals because of their charge and / or size (De Hoog et al., 2010).

Olivine has been used as a tar removal catalyst in a sewage sludge gasification process (De Andrés et al., 2011; Miccio et al., 2009). Because of the high melting temperature and the deposits being of non-gem quality, olivine has been used in the manufacture of high temperature refractory bricks and insulation boards (King, 2009).

The metamorphosis (altered) products include serpentine minerals, clay minerals (including chlorite, amphiboles, and talc), carbonates and pseudomorphic goethite compounds. Olivine has independent SiO$_4$ tetrahedra and is prone to hydrothermal alteration, due to geothermal reaction in rock.
The composition is presented in equations 3 and 4 (King, 2009):

\[
2Mg_2SiO_4 + 2H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + MgO \quad \text{Equation 2}
\]

forsterite + water \( \rightarrow \) serpentine + MgO

or

\[
3Mg_2SiO_4 + SiO_2 \cdot 4H_2O \rightarrow 2Mg_3Si_2O_5(OH)_4 \quad \text{Equation 3}
\]

forsterite + silica + water \( \rightarrow \) serpentine

Forsterite is the Mg-rich end member of olivine materials and serpentine is a hydrous magnesium-iron phyllosilicate.

The characteristics of the olivine rich materials (Blueguard\textsuperscript{®} materials) used in this work are given in Chapter 2. The material is on the Mg rich end of the scale. Figure 1-8 shows the structure of magnesium rich olivine, taken from the Inorganic Crystal Structure Database (ICSD). By comparing powder X-ray diffraction (XRD) data (section 2.4) to the information from the ICSD, it is evident that this structure is consistent with the materials in this work.

![Figure 1-8 Structure of olivine (www.4), Key: brown spheres are Mg, white Si and red O atoms](image)

1.5 Biological Unit Operation

A biological treatment process is employed to remove biodegradable organic matter, nutrients and suspend solids (Ranade, 2014) and is usually used in secondary treatment processes (Figure 1-4). This system uses microorganisms to degrade and decompose organic material during treatment under aerobic or anaerobic conditions.
The aerobic treatment process as shown in Figure 1-9, involves aerobic (presence of air) digestion. The reaction products of this process are carbon dioxide and water. The major disadvantage of an aerobic system is the large amount of biomass produced due to the aerobic nature of this process (Ranade & Bhandari, 2014).

![Figure 1-9 Schematic of anaerobic biological treatment (Ranade & Bhandari, 2014)](image1)

In an anaerobic digestion system, organic matter is decomposed by a variety of microbes. This biological process can take place naturally or in a controlled environment, such as a biogas plant. The anaerobic process takes place in the absence of air and the biogas of this process contain methane and carbon dioxide (Figure 1-10). The growth of microorganisms involved in an anaerobic process depends on factors, such as, pH, residence time, temperature, redox potential and nutrient composition (Ranade & Bhandari, 2014).

![Figure 1-10 Schematic of anaerobic biological treatment (Ranade & Bhandari, 2014)](image2)
Biological treatment systems can also be further categorised, as below:

(1) lagoons and ponds, which are slow, cheap and relatively inefficient when used separately. However, when combined with other conventional processes like secondary or tertiary treatments, these systems can be efficient. The interaction of sunlight, algae, microorganisms and oxygen in these systems can improve the biological condition of wastewater (Krantzberg et al., 2010);

(2) constructed and natural wetlands, which provide a high degree of aerobic biological improvement and can often be used instead of secondary treatment for small communities (Krantzberg et al., 2010). Both types of wetlands have one characteristic in common which is the presence of surface or near-surface water (at least periodically). Wetlands are constructed using substrates, such as, soil, sand, gravel, rock and organic materials, such as compost. Such a substrate provides storage for various contaminants and many chemical and biological (especially microbial) transformations take place within these substrates (Alley, 2007).

1.6 Aims and Objectives of This Research

The main aim of this research was to conceive a novel method, and engineered solution, for removing chemical contaminants from main sources of water pollution, namely, point (industrial discharge) and non-point (stormwater run-off). In this study this has been achieved by the following objectives:

(1) the ability of Blueguard® materials to remove trace elements from laboratory prepared contaminated water
This solution was used to investigate the ability and efficiency of Blueguard® materials in removing trace elements from contaminated water as would be required for application in the real world;

(2) the application of Blueguard® materials for the removal of trace elements from real world contaminated water samples
As the real world is different to ideal laboratory conditions, experiments were required to explore the efficiency of Blueguard® materials in removing trace elements from contaminated water coming from different origins and therefore chemistry. Optimisation of the use of these materials allows for a more efficient use in different areas of application;
(3) the applicability of Blueguard® materials for cleaning-up industrial discharge under ‘real’ field-based conditions (an engineered solution)

The ability to apply the materials on-site using field based remediation solutions was the final goal to show the true potential of this material; and

(4) investigating the removal mechanism of Blueguard® materials

It is important to know the mechanism whereby these materials function and to ensure that the possible remediation effect cannot be attributed to other processes.
Chapter 2 Experimental Methods and Material Characterisation

2.1 Introduction
In this chapter, novel mineral based materials provided by Sibelco (Blueguard® materials) are introduced and characterised in terms of structure and properties. The characterisation techniques applied in this research include X-ray powder diffraction (XRD), X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) which were used to reveal the crystal structure and elemental analysis/composition of these materials and possible changes after contact with the solutions under investigation. Furthermore, scanning electron microscopy (SEM) was used to probe and map the surface of the material, along with Brunauer–Emmett–Teller (BET) sorptiometry, which measures the specific surface area of a powder.

The analysis results and interpretation are then discussed to understand the structure and properties, and subsequently the application of the materials in possible wastewater treatment.

2.2 Olivine-rich Materials (Blueguard®)
The material used in this study (Blueguard®) is a dunite rock source (it is peridotite ultramafic rock with > 90% olivine) and was provided by Sibelco Nordic Deposits of Åheim, Norway. The rock was dug, crushed and then transported to the processing plant where it was broken into its natural agglomerate size pieces. The resultant material was enriched with auxiliary minerals, such as, talc, lizardite, and chlorite.

In this project three different types of the Blueguard® materials have been studied to investigate the applicability of these materials as a solid phase material for the remediation of wastewaters associated with different chemically contaminated sites. The main chemicals under investigation are trace elements (defined as elements at concentrations typically less than 100 mg l⁻¹), or in some cases they are referred to as heavy metals (based on density). These materials are commercially labelled as Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C.
Blueguard® 63 is a fine grained mineral (flour texture), whereas Blueguard® G1-3 and Blueguard® G1-3C are granulated forms of Blueguard® 63. Blueguard® G1-3C is the same as Blueguard® G1-3 except that it has an addition of activated carbon.

It is necessary to know the distribution of particle sizes of the material in order to provide proper contact of liquid in a packed bed of the material. Therefore, the size and the degree of fineness of Blueguard® (particle size distribution) are presented in Table 2-1. The particle size, $D_{50}$, is defined as the grain diameter for which 50% of the sample is finer than the rest. Sizes $D_{10}$ and $D_{90}$ are associated with 10% and 90% finer limits. Therefore 50% of the particles in Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C are finer than 0.025, 2.5 and 2.5 mm, respectively. 90% of the particles in Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C are finer than 0.063, 2.5 and 2.5 mm, respectively. Only 10% of the particles in Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C are finer than 0.006, 1.0 and 1.0 mm, respectively.

The effect of Blueguard® materials on pH was also investigated using deionised distilled water (DDW). The pH value of DDW (from the initial value of 7) after contact with Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C increases to 10 and 11 and11, respectively, suggesting these materials release hydroxide ions (as OH$^-$(aq)) into the solution.

Characterisation techniques were applied in order to understand the structure and properties of the Blueguard® materials, as well as justifying the mechanism by which these materials remove trace elements from a wastewater solution.

**Table 2-1 Particle size distribution of Blueguard® materials (mm)**

<table>
<thead>
<tr>
<th>% passing sieve</th>
<th>Size distribution</th>
<th>Blueguard® 63</th>
<th>Blueguard® G1-3</th>
<th>Blueguard® G1-3C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{90}$</td>
<td>0.063 mm</td>
<td>2.5 mm</td>
<td>2.5 mm</td>
<td></td>
</tr>
<tr>
<td>$D_{50}$</td>
<td>0.025 mm</td>
<td>2.5 mm</td>
<td>2.5 mm</td>
<td></td>
</tr>
<tr>
<td>$D_{10}$</td>
<td>0.006 mm</td>
<td>1.0 mm</td>
<td>1.0 mm</td>
<td></td>
</tr>
</tbody>
</table>

$D_{90}$ = smallest sieve opening through which 90% or more of the material passes
$D_{50}$ = smallest sieve opening through which 50% or more of the material passes
$D_{10}$ = smallest sieve opening through which 10% or more of the material passes
2.3 X-ray Fluorescence Spectrometry (XRF)

X-ray fluorescence (XRF) is a spectrometric technique which measures the emission of characteristic X-rays that occurs when atoms are excited by an external source of X-rays. When an external source of X-ray radiation strikes a sample, inner shell electrons are ejected and an outer shell electron replaces the missing inner electron. This process gives off a characteristic X-ray, unique to this element, whose energy is the difference between the two binding energies of the corresponding shells (Figure 2-1). The resulting fluorescent X-rays can be used to detect the abundances of elements present in the sample (Shackley, 2011).

![Figure 2-1 Schematic of the interaction of incident X-rays and electrons in a sample (www.5)](image)

2.3.1 Experimental aspects and sample preparation

Chemical composition analysis of the Blueguard® materials provided by Sibelco was carried out by British Geological Survey (BGS) using a PANalytical Axios mAX sequential, fully automatic wavelength-dispersive X-ray fluorescence spectrometer, fitted with an automatic sample changer of 136 samples capacity. The spectrometer was fitted with a 60 kV generator and 4 kW rhodium (Super Sharp) end–window X-ray tube. The software used to control the instrument and report data was PANalytical SuperQ 5.1B.

2.3.2 Analysis of the Materials

The results obtained from XRF analysis (Table 2-2) of all three forms of Blueguard® are in line with the findings previously obtained from XRD analysis.
The results confirm that magnesium iron silicate of formula (Mg, Fe)$_2$SiO$_4$, is the major compound and provides the main elements available in these materials. XRF data reveals that Blueguard® G1-3 and Blueguard® G1-3C contain a higher level of calcium compared to the powder form of Blueguard® 63. This is due to Ca-containing binders that have been used to alter the Blueguard® 63 to the granular forms.

### Table 2-2 Elemental composition (%) of Blueguard® in this work, as determined by BGS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Blueguard® G1-3 Mass (%)</th>
<th>Blueguard® G1-3C Mass (%)</th>
<th>Blueguard® 63 Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>39.36</td>
<td>39.78</td>
<td>41.72</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.49</td>
<td>0.55</td>
<td>0.88</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>6.47</td>
<td>6.44</td>
<td>6.62</td>
</tr>
<tr>
<td>Mn$_3$O$_4$</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>MgO</td>
<td>44.47</td>
<td>44.91</td>
<td>46.21</td>
</tr>
<tr>
<td>CaO</td>
<td>5.03</td>
<td>4.75</td>
<td>0.32</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.03</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.03</td>
<td>0.03</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.26</td>
<td>0.30</td>
<td>0.40</td>
</tr>
<tr>
<td>SrO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>BaO</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>NiO</td>
<td>0.32</td>
<td>0.32</td>
<td>0.34</td>
</tr>
<tr>
<td>CuO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>PbO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>F</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>LOI$^1$</td>
<td>4.27</td>
<td>3.56</td>
<td>4.17</td>
</tr>
</tbody>
</table>

$^1$Loss on ignition

### 2.4 X-ray Powder Diffraction (XRD)

X-ray diffraction analysis of a sample can help to determine the structure and whether there are any impurities in the sample. The diffraction data that are
obtained will depend on the crystal structure the sample adopts. The result depends on the lattice type, crystal class and unit cell parameters (Weller, 2001).

X-ray diffraction works by using X-rays, of a fixed wavelength and at varying incident angle, directed through a crystal such that the X-rays are diffracted. In terms of Bragg diffraction (Weller, 2001), the scattered X-ray leaves the crystal at an angle equal to that of the incident beam. This is shown in Figure 2-2, where, \( d \) is the crystal lattice planar separation, \( ABC \) and \( A'B'C' \) define the path, with length of the X-ray paths; the difference between the two paths is an integer multiple of the wavelength \( \lambda \).

![Figure 2-2 Illustration of Bragg's Law (Weller, 2001)](image)

In describing the process of X-ray diffraction of solids, Bragg considered the crystal structures as being built up of lattice planes. Bragg’s Law states:

\[
2d \sin\theta = n \lambda 
\]

Equation 4

where \( n \) is the order of the reflection (normally set to 1), \( \lambda \) is the wavelength of radiation used, \( d \) is the inter-planar spacing, and \( \theta \) is the diffraction angle. Bragg’s law means that the inter-planar spacing between the crystal lattice planes can be determined from the diffraction pattern (Weller, 2001).

The diffraction pattern is produced when the X-rays interact with the electrons in the material and are then scattered. The detector will measure the intensity of the diffracted X-rays and this is plotted against \( 2\theta \). During the analysis the detector, X-ray source and the sample move relative to one another to ensure the focusing of the X-ray beam, as seen in Figure 2-3 (Heap, 2006).
2.4.1 Experimental and sample preparation

The XRD instrument used in this research project was a PANalytical X’Pert Pro instrument and the programme used to analyse the data is PANalytical High Score Plus version 3.0d (3.0.4). Sample preparation was carried out by grinding a few grams of Blueguard® G1-3 and Blueguard® G1-3C to a fine powder of less than ~10 µm in particle size (Blueguard® 63 did not require this as it was already a fine powder). The samples were then placed into sample holders with extra care to create a flat upper surface. Each individual sample was analysed and the d-spacing associated with each peak was obtained by applying the Bragg equation, for the appropriate value of λ; the 2θ range was 0-90° and a total run time of 1 h 20 min. The diffraction patterns were recorded at room temperature using CuKα radiation (λ = 1.54055 Å) at a scanning speed of 4 deg. min−1 and a step size of 0.02° (2θ). Once all d-spacings were determined, automated search / match routines compare the d’s of the unknown to those of known materials which are available in the International Centre for Diffraction Data (ICDD) database. As each mineral has a unique set of d-spacings, matching these d-spacings with the known ones provided an identification of the unknown compounds in the sample. Results of this experiment are presented in Table 2-3. The X ray diffraction pattern of all three kinds of Blueguard® are shown as X-ray count (intensity) peak positions at varying 2θ (intensity), in Figure 2-4.
2.4.2 Analysis of the materials

Figure 2-4 shows the series of Blueguard® materials have various phases and (ICDD) confirms the presence of different compounds which are detailed in Table 2-3 and Figure B-1. This confirms that the XRD peak positions and diffraction data for all three types of Blueguard® materials are near identical, varying only with additions. This can be seen more clearly in the zoomed version of the same results in the range $40 < 2\theta / \text{deg} < 60$ shown in Figure 2-5, suggesting the materials have near identical mineral composition.
The specific surface area of a powder can be determined by using the Brunauer–Emmett–Teller (BET) technique. BET is based on the physical adsorption of a gas (N\textsubscript{2}(g) here) on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. The adsorbent is exposed and allowed to reach equilibrium with an adsorptive gas at pressure \( p \), where an amount of gas adsorbs on the surface and compared to saturation pressure \( p^\circ \). The saturation pressure is recorded at the beginning of each analysis period. The concept of the BET theory is an extension of the Langmuir theory with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer. Equation 5 gives the most convenient form of the BET equation for experimental application:

\[
\frac{p}{p^\circ} \frac{n}{n_m C} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} \left(\frac{p}{p^\circ}\right) \quad \text{Equation 5}
\]

where \( p \) and \( p^\circ \) are the equilibrium and the saturation pressure (Pa) of adsorbates at the temperature of adsorption, \( n \) is the adsorbed gas quantity (for example, in volume units), and \( n_m \) is the monolayer adsorbed gas quantity. \( C \) is the BET constant,

\[
C = \exp \left(\frac{E_1 - E_2}{RT}\right) \quad \text{Equation 6}
\]

\( E_1 \) is the heat of adsorption for the first layer, and \( E_2 \) is for the second and higher layers and is taken to be equal to the heat of liquefaction, \( R \) is the gas constant and \( T \) is absolute temperature (kelvin).

### Table 2-3 Mineral phases in Blueguard\textsuperscript{®} materials in this work

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Formula</th>
<th>System</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>alpha</th>
<th>beta</th>
<th>gamma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>(Mg\textsubscript{1.86}Fe\textsubscript{0.14})(SiO\textsubscript{4})</td>
<td>Orthorhombic</td>
<td>4.757</td>
<td>10.212</td>
<td>5.984</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Talc</td>
<td>Mg\textsubscript{2}Si\textsubscript{2}O\textsubscript{10}(OH)\textsubscript{2}</td>
<td>Monoclinic</td>
<td>5.287</td>
<td>9.171</td>
<td>18.964</td>
<td>90</td>
<td>99.61</td>
<td>90</td>
</tr>
<tr>
<td>Clinohlore</td>
<td>Mg\textsubscript{2}Al(Si\textsubscript{2}O\textsubscript{10})(OH)\textsubscript{8}</td>
<td>Triclinic</td>
<td>5.317</td>
<td>9.227</td>
<td>14.324</td>
<td>90.3</td>
<td>97.3</td>
<td>89.9</td>
</tr>
<tr>
<td>Antigorite</td>
<td>Mg\textsubscript{2}Si\textsubscript{2}O\textsubscript{10}(OH)\textsubscript{8}</td>
<td>Monoclinic</td>
<td>43.522</td>
<td>9.253</td>
<td>7.262</td>
<td>90</td>
<td>91.32</td>
<td>90</td>
</tr>
<tr>
<td>Biotite</td>
<td>K(Mg\textsubscript{3}Fe\textsuperscript{3+})(Al,Fe\textsuperscript{3+})Si\textsubscript{3}O\textsubscript{10}(OH,F)</td>
<td>Monoclinic</td>
<td>5.344</td>
<td>9.252</td>
<td>10.228</td>
<td>90</td>
<td>100.18</td>
<td>90</td>
</tr>
<tr>
<td>Ferroactinolite</td>
<td>(Ca,Na,K)\textsubscript{2}Fe\textsubscript{5}Si\textsubscript{8}O\textsubscript{22}(OH)\textsubscript{2}</td>
<td>Monoclinic</td>
<td>9.753</td>
<td>18.009</td>
<td>5.326</td>
<td>90</td>
<td>103.6</td>
<td>90</td>
</tr>
</tbody>
</table>
Gas adsorption experiments on porous materials yield different isotherm curves. These curves have been classified into six isotherm types which are shown in Figure 2-6 and Table 2-4. This classification is defined by the International Union of Pure and Applied Chemistry (IUPAC) based on known experimental behaviour.

![Figure 2-6 Classification of BET adsorption isotherms (Thommes 2015)](image)

Table 2-4 Classification of BET adsorption isotherms (Balbuena and Gubbins 1993)

<table>
<thead>
<tr>
<th>Type</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Microporous or non-porous</td>
</tr>
<tr>
<td>II</td>
<td>Mainly non-porous or macroporous</td>
</tr>
<tr>
<td>III</td>
<td>Non-porous, weak adsorbent-adsorbate interactions</td>
</tr>
<tr>
<td>IV</td>
<td>Mesoporous, usually micropores, hysteresis on desorption</td>
</tr>
<tr>
<td>V</td>
<td>Mesoporous or macroporous, hysteresis on desorption, weak adsorbent adsorbate interactions</td>
</tr>
<tr>
<td>VI</td>
<td>Multi-layered sorption</td>
</tr>
</tbody>
</table>

### 2.5.1 Experimental aspects and sample preparation

Specific surface-areas \( (m^2 \text{ g}^{-1}) \) were determined using Micromeritics FlowPrep 060 and Micrometrics Gemini V Surface Area and Pore Size Analyser (Figure 2-7). The initial weight of all three types of Blueguard® material was recorded (0.5 g) and outgassed at 200ºC for 12 hours, so as to remove water and other contaminants before the surface area could be accurately measured.
Saturation pressure, as the first step of the analysis, was measured using a clean and empty sample test-tube which was evacuated of air and replaced with nitrogen using a dewar vessel containing liquid nitrogen, cooled to 77 K (Figure 2-7). The pressure of this tube was recorded as saturated pressure ($p^\circ$). Next sample test-tubes to be filled with outgassed samples were selected and the pressure of these samples in the tubes were then measured ($p$). The relative pressure was then calculated as $\frac{p}{p^\circ}$; and the complete set of results of sorption desorption were obtained (Roberts and Slade, 2010).

2.5.2 Gas sorption analysis of the materials

The resulting isotherms for Blueguard® materials demonstrate mainly non-porous or macroporous classification for Blueguard® 63 and Blueguard® G1-3. Blueguard® G1-3C would fall into classification of IV, suggesting mesoporous, with some micropores and hysteresis on desorption. This change, relative to Blueguard® 63 and Blueguard® G1-3 is due to the addition of activated carbon in Blueguard® G1-3C (Figure 2-8).
2.6 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is applied to observe and examine the surface structure of sample materials both for organic and inorganic components, at nanometre (nm) to micrometre (µm) scales (Goldstein et al., 2003). In this technique, the area to be imaged or analysed is irradiated with a focused electron beam. The electrons in the beam interact with the electrons in surface atoms. This interaction produces various signals that can be detected and that contain information about the sample's surface topography and chemical composition (Goldstein et al., 2003).
The components of an SEM are shown in Figure 2-9. The electron gun produces electrons by applying thermal energy to a filament which is directed at the sample placed within a sample chamber. Lenses are applied to focus and control the electron beam, ensuring that the electrons end up precisely where they need to go. Sample chambers are used to manipulate the specimen, placing it at different angles and moving it, so that there is no need to constantly remount the object to take different images. The secondary detector registers secondary electrons which are dislodged from the outer surface of a specimen. These detectors are capable of producing the most detailed images of an object's surface. Other detectors, such as backscattered electron detectors and X-ray detectors, can inform researchers about the chemical composition of a substance (www.7).

The vacuum chamber stops interference (scattering from gas atoms otherwise in the SEM) which can block the path of the electron beams in the chamber. This also prevents the distortion of the beam path.

### 2.6.1 Experimental and sample preparation
All samples were gold coated to a depth of 2 nm using the Emitech K57X peltier cooler spotter and were viewed in the secondary electron emission mode of a JEOL JSM 7100F scanning electron microscope at an accelerating voltage of 5 kV.

### 2.6.2 Analysis of the materials
Visual examinations of the Blueguard\textsuperscript{®} materials are shown in Figure 2-10. All three types of this mineral-based material contain sharp angles with similar rough and uneven surface morphology, as well as agglomeration particles on the surface. Blueguard\textsuperscript{®} 63 showed a clearer and more even surface while Blueguard\textsuperscript{®} G1-3 and Blueguard\textsuperscript{®} G1-3C showed an increase in the number of smaller particles and an increase in angularity.
2.7 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Techniques for the analysis of trace elements are required to determine the unknown concentration of an element. A variety of advanced techniques can be applied to measure trace elements: electrochemical techniques, such as, ion-selective electrodes (ISEs); atomic spectrometric methods, including flame atomic absorption spectrometry (FAAS), inductively coupled plasma - atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS); X-ray and nuclear techniques (Brown and Milton 2005). Inductively coupled plasma mass spectrometry (ICP-MS) is a multi-element technique, based on measuring the mass-to-charge (m/z) ratios of elements, and is used to determine the concentration of trace elements in a sample (Ammann, 2007). ICP-MS has many advantages including extremely low limits of detection (typically < 0.1 µg l⁻¹), a wide linear dynamic range (typically 10⁸ orders of magnitude), multi-element capability and high sample throughput (Cornelis & Nordberg, 2007). The inductively coupled plasma (ICP) is at approximately 7000 K, which converts the sample into ions (positively single charged ions X⁺) which
are then separated using a quadrupole mass filter and detected by a channel electron multiplier detector (Dean, 2004).

As shown in Figure 2-11 the principle features of an ICP-MS instrument consist of (i) the inductively coupled plasma ion source (ICP) for the desolvation, dissociation, atomisation and ionisation of the sample, (ii) the analyser (quadrupole) for the mass (and energy) separation of ions that are extracted from the ion source via the interface, and (iii) the ion detection system (electron multiplier) (Becker, 2002).

![Figure 2-11 Schematic of the Surrey ICP-MS Facility Agilent 7700 Series inductively coupled plasma mass spectrometer used in this research (Agilent, 2012)](image)

2.7.1 ICP-MS Methodology

The ICP-MS instrument used in this study was an Agilent 7700x Series (Agilent, UK) with an ASX-500 series auto sampler (Agilent, UK). The typical instrumental operating conditions are shown in Table 2-5.
Table 2-5 Typical operating parameters for the Agilent 7700x ICP-MS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Typical operating condition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample introduction</strong></td>
<td></td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>0.8 l min⁻¹</td>
</tr>
<tr>
<td>Make-up gas flow rate</td>
<td>0.3 l min⁻¹</td>
</tr>
<tr>
<td>Nebuliser pump</td>
<td>0.1 rps</td>
</tr>
<tr>
<td>Spray chamber temperature</td>
<td>2 °C</td>
</tr>
<tr>
<td><strong>Plasma condition</strong></td>
<td></td>
</tr>
<tr>
<td>RF Power</td>
<td>1550 W</td>
</tr>
<tr>
<td>RF Matching</td>
<td>1.95 V</td>
</tr>
<tr>
<td>Sampling Depth</td>
<td>8 mm</td>
</tr>
<tr>
<td>Plasma gas flow rate</td>
<td>15 l min⁻¹</td>
</tr>
<tr>
<td>Auxiliary gas flow rate</td>
<td>0.9 l min⁻¹</td>
</tr>
<tr>
<td>Collision/reaction cell</td>
<td>He mode</td>
</tr>
<tr>
<td>[1] ON</td>
<td></td>
</tr>
<tr>
<td>He gas flow rate</td>
<td>4.8 ml min⁻¹</td>
</tr>
<tr>
<td>Analyte isotopes</td>
<td>$^{27}$Al, $^{52}$Cr, $^{63}$Cu, $^{56}$Fe, $^{39}$K, $^{24}$Mg, $^{55}$Mn, $^{23}$Na, $^{60}$Ni, $^{208}$Pb and $^{66}$Zn</td>
</tr>
<tr>
<td><strong>Detector</strong></td>
<td></td>
</tr>
<tr>
<td>Pulse HV</td>
<td>980 V</td>
</tr>
<tr>
<td>Analog HV</td>
<td>1680 V</td>
</tr>
<tr>
<td><strong>Data acquisition</strong></td>
<td></td>
</tr>
<tr>
<td>Sample uptake time</td>
<td>50 s</td>
</tr>
<tr>
<td>Wash time between samples</td>
<td>120 s</td>
</tr>
</tbody>
</table>

In this research a series of multi-element calibration solutions ranging from 0.1 to 750 µg l⁻¹ of $^{27}$Al, $^{52}$Cr, $^{63}$Cu, $^{56}$Fe, $^{55}$Mn, $^{60}$Ni, $^{208}$Pb and $^{66}$Zn and from 1 to 2000 µg l⁻¹ of $^{43}$Ca, $^{39}$K, $^{24}$Mg, $^{23}$Na, were run on the ICP-MS instrument along with an internal standard solution of 100 µg l⁻¹ of $^{72}$Ge, $^{103}$Rh and $^{45}$Sc, (used to check for instrument variations caused by matrix interferences) (Farnfield, 2012). Analyte elements (and isotopes) of interest, their natural abundances and some polyatomic interference are listed in Table 2-6. These species may form through matrix / solvent / plasma combinations and interfere with the measurement of the analyte ions of interest (Taylor, 2001). The raw data (counts per second) were blank corrected, ratioed with the selected internal standard signal and plotted as the ratio of the two signals (y-axis) versus the elemental concentrations (x-axes). From the calibration curve, the equation of the line was used to calculate the concentration of the sample solution under investigation (Figures A-1 and A-2).
**Table 2-6 Elements (isotopes) of interest, related natural abundances and some polyatomic interferences that may overlap the isotope signals (Vandecasteele and Block 1997)**

<table>
<thead>
<tr>
<th>Analyte Isotope*</th>
<th>Abundance (%)</th>
<th>Polyatomic Interference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{27}$Al$^+$</td>
<td>100</td>
<td>$^{12}$C$^{15}$N$^+$, $^{13}$C$^{14}$N$^+$, $^{14}$N$^2$ $^{1}$H$^{12}$C$^{14}$N$^+$</td>
</tr>
<tr>
<td>$^{43}$Ca$^+$</td>
<td>0.145</td>
<td>$^{27}$Al$^{16}$O$^+$</td>
</tr>
<tr>
<td>$^{52}$Cr$^+$</td>
<td>83.76</td>
<td>$^{35}$Cl$^{16}$O$^+$H$^+$, $^{40}$Ar$^{12}$C$^+$, $^{36}$Ar$^{16}$O$^+$, $^{37}$Cl$^{15}$N$^+$, $^{34}$S$^{18}$O$^+$, $^{36}$S$^{16}$O$^+$, $^{38}$Ar$^{14}$N$^+$, $^{36}$Ar$^{15}$N$^1$H$^+$, $^{35}$Cl$^{17}$O$^+$</td>
</tr>
<tr>
<td>$^{63}$Cu$^+$</td>
<td>69.10</td>
<td>$^{31}$P$^{18}$O$^{2+}$, $^{40}$Ar$^{23}$Na$^+$, $^{23}$Na$^{40}$Ca$^+$, $^{46}$Ca$^{16}$O$^1$H$^+$</td>
</tr>
<tr>
<td>$^{56}$Fe$^+$</td>
<td>91.66</td>
<td>$^{40}$Ar$^{16}$O$^+$, $^{40}$Ca$^{16}$O$^+$, $^{40}$Ar$^{15}$N$^1$H$^+$, $^{38}$Ar$^{18}$O$^+$</td>
</tr>
<tr>
<td>$^{39}$K$^+$</td>
<td>93.08</td>
<td>$^{38}$Ar$^{1}$H$^+$</td>
</tr>
<tr>
<td>$^{24}$Mg$^+$</td>
<td>79.00</td>
<td>$^{12}$C$^2$H$^+$, CN$^+$, NaH$^+$</td>
</tr>
<tr>
<td>$^{55}$Mn$^+$</td>
<td>100.00</td>
<td>$^{40}$Ar$^{15}$N$^1$H$^+$, $^{38}$Ar$^{18}$O$^+$, $^{40}$Ar$^{10}$O$^{1+}$H$^+$, $^{37}$Cl$^{18}$O$^+$</td>
</tr>
<tr>
<td>$^{23}$Na$^+$</td>
<td>100.00</td>
<td>$^{12}$C$^2$H$^+$, CN$^+$, NaH$^+$</td>
</tr>
<tr>
<td>$^{60}$Ni$^+$</td>
<td>26.16</td>
<td>$^{44}$Ca$^{16}$O$^+$, $^{23}$Na$^{37}$Cl$^+$, $^{43}$Ca$^{16}$O$^{1+}$H$^+$</td>
</tr>
<tr>
<td>$^{208}$Pb$^+$</td>
<td>52.4</td>
<td>$^{192}$Pb$^{16}$O$^+$</td>
</tr>
<tr>
<td>$^{66}$Zn$^+$</td>
<td>27.81</td>
<td>$^{34}$S$^{16}$O$^{2+}$, $^{32}$S$^{34}$S$^+$, $^{33}$S$^{2+}$</td>
</tr>
</tbody>
</table>

*a collision cell was used in a positive mode to correct for all possible polyatomics

Many of the possible polyatomic interferences listed in Table 2-6 are not relevant (e.g. those associated with sulphur (H$_2$S and (SO$_4$)$_2^-$) are not detectable in the materials or samples). Throughout the sample analysis the Agilent 7700x run produce uses an octapole collision cell with the gas addition (gas mode (He)) to correct for any possible polyatomics below 82 m/z.

The limit of detection (LoD) is defined as the lowest concentration of an analyte in a sample that can be detected by the instrument but can be reliably distinguished from the blank signal (Shrivastava & Gupta, 2011). The LOD can be calculated using the following equation:

$$ LoD = SB + (3 \times SD) $$

*Equation 7*

where, SB is the mean blank signal, SD is the standard deviation of the blank signal (Miller & Miller, 1993). Table 2-7 reports the limit of detection (µg l$^{-1}$) for selected trace elements using a blank solution, namely distilled deionised water (DDW, 18.2 MΩ).
Table 2-7 Limit of detection (LoD) for selected trace elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass to charge ratio (m/z)</th>
<th>Internal Standard (IS)</th>
<th>Gas Mode</th>
<th>LoD (µg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>27</td>
<td>⁴⁵Sc⁺</td>
<td>He</td>
<td>0.6</td>
</tr>
<tr>
<td>Ca</td>
<td>43</td>
<td>⁴⁵Sc⁺</td>
<td>He</td>
<td>12</td>
</tr>
<tr>
<td>Cd</td>
<td>111</td>
<td>⁴⁵Sc⁺</td>
<td>He</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>52</td>
<td>⁴⁵Sc⁺</td>
<td>He</td>
<td>0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>63</td>
<td>⁷²Ge⁺</td>
<td>He</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>56</td>
<td>⁴⁵Sc⁺</td>
<td>He</td>
<td>0.2</td>
</tr>
<tr>
<td>K</td>
<td>39</td>
<td>⁴⁵Sc⁺</td>
<td>He</td>
<td>4</td>
</tr>
<tr>
<td>Mn</td>
<td>55</td>
<td>⁴⁵Sc⁺</td>
<td>He</td>
<td>0.01</td>
</tr>
<tr>
<td>Mg</td>
<td>79</td>
<td>⁴⁵Sc⁺</td>
<td>He</td>
<td>0.4</td>
</tr>
<tr>
<td>Na</td>
<td>23</td>
<td>⁴⁵Sc⁺</td>
<td>He</td>
<td>32</td>
</tr>
<tr>
<td>Ni</td>
<td>60</td>
<td>⁴⁵Sc⁺</td>
<td>He</td>
<td>0.09</td>
</tr>
<tr>
<td>Pb</td>
<td>208</td>
<td>²⁰⁹Bi⁺</td>
<td>no gas</td>
<td>0.01</td>
</tr>
<tr>
<td>Zn</td>
<td>66</td>
<td>⁷²Ge⁺</td>
<td>He</td>
<td>1</td>
</tr>
</tbody>
</table>

2.7.2 Accuracy and precision

Quality control is important in terms of checking the performance of the ICP-MS. Accuracy is the closeness of agreement between the measured mean of replicate analyses with a ‘true’ value (or certified value for a certified reference material) (Miller & Miller, 2000). Precision or repeatability is a measure of how close the values are for replicate analysis of a solution under the same instrumental conditions and is determined by calculation of the relative standard deviation (and reported as a %) (Miller & Miller, 1993). The instrumental levels of accuracy and precision were determined using two certified reference materials (CRMs), namely Trace Elements in Water 1640a (National Institute of Standards, Gaithersburg, USA) and a Trace Element Fortified Water Sample TMDA 54.5 (Environment Canada). Accuracy was estimated by comparing the mean calculated value for an element against the certified value for the specific CRM. For example, for zinc replicate analysis of CRM 1640a (n = 6) gave a mean value of 54.6 µg l⁻¹ Zn which provides an accurate comparison with the certified value of 55.64 µg l⁻¹ Zn. A paired t-test statistical calculation was performed using Prism
Pad™ for the various trace elements determined in both certified reference materials. For 8 degrees of freedom, the $t_{\text{crit}}$ value is 2.306 (probability $p<0.05$, confidence interval 95%). The calculated $t_{\text{cal}}$ values for CRM 1640a ($t_{\text{cal}} = 1.920$) and TMDA 54.5 ($t_{\text{cal}} = 0.7892$) are both lower than the $t_{\text{crit}}$ value (2.306), confirming that there is no statistically significant difference between the measured and certified values. This supports the good levels of accuracy for the determination of trace element levels in water samples using the ICP-MS procedure already outlined in this chapter.

The levels of repeatability (precision) were calculated from the relative standard deviation (RSD) of replicate measurements of the CRM e.g. for Zn for $n = 6$ replicates of the CRM 1640a solution the RSD = 0.5%, which is an acceptable level of precision. This is also confirmed for the other elements with the range of RSD values being 0.01 to 3.5%.

Once use of the ICP-MS instrument had been validated (refer to Table 2-8), all of the solutions for later use in batch equilibrium experiments were analysed using these procedures outlined above.

### Table 2-8 Validation of accuracy and precision levels for the multi-element analysis of water samples by ICP-MS. Analysis of certified reference materials reported as a mean ± standard deviation; $n$ is number of measurements, RSD (%) relative standard deviation

<table>
<thead>
<tr>
<th>Elements</th>
<th>m/z</th>
<th>Certified</th>
<th>Measured ($n=6$)</th>
<th>% RSD ($n=6$)</th>
<th>Certified</th>
<th>Measured ($n=6$)</th>
<th>% RSD ($n=6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>27</td>
<td>53.0 ± 1.8</td>
<td>53.01±0.02</td>
<td>0.04</td>
<td>400 ± 35</td>
<td>403.0±6.50</td>
<td>1.6</td>
</tr>
<tr>
<td>Cd</td>
<td>111</td>
<td>3.992 ± 0.074</td>
<td>6.23 ± 0.06</td>
<td>1.0</td>
<td>158 ± 10</td>
<td>164.9±0.98</td>
<td>0.6</td>
</tr>
<tr>
<td>Cr</td>
<td>52</td>
<td>40.5 ± 0.30</td>
<td>40.30 ± 0.07</td>
<td>0.2</td>
<td>438 ± 32</td>
<td>456 ± 9.50</td>
<td>2.1</td>
</tr>
<tr>
<td>Cu</td>
<td>63</td>
<td>85.75 ± 0.51</td>
<td>87.60 ± 0.13</td>
<td>0.1</td>
<td>414 ± 38</td>
<td>423.7±14.9</td>
<td>3.5</td>
</tr>
<tr>
<td>Fe</td>
<td>56</td>
<td>36.8 ± 1.8</td>
<td>38.90 ± 0.25</td>
<td>0.6</td>
<td>383 ± 34</td>
<td>395.7±9.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Mn</td>
<td>55</td>
<td>40.39 ± 0.36</td>
<td>41.80 ± 0.23</td>
<td>0.6</td>
<td>284 ± 23</td>
<td>272.8±6.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Ni</td>
<td>60</td>
<td>25.32 ± 0.14</td>
<td>27.30 ± 0.08</td>
<td>0.3</td>
<td>335 ± 25</td>
<td>342 ± 9.8</td>
<td>2.9</td>
</tr>
<tr>
<td>Pb</td>
<td>208</td>
<td>12.101 ± 0.050</td>
<td>11.40 ± 0.08</td>
<td>0.7</td>
<td>515 ± 39</td>
<td>231.5±1.54</td>
<td>0.7</td>
</tr>
<tr>
<td>Zn</td>
<td>66</td>
<td>55.64 ± 0.35</td>
<td>54.60 ± 0.25</td>
<td>0.5</td>
<td>545 ± 49</td>
<td>552.4±1.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

#### 2.7.3 Evaluation of the elemental release from Blueguard® materials

An initial study was undertaken to evaluate what elements are released form the Blueguard® materials on contact with water. This is important so as to know what possible elements may be released into solution depending on the ‘purity’ of the materials obtained from Sibelco Ltd. This experiment was carried out by mixing
0.5 g of the materials with 50 ml distilled deionised water (DDW) (the same source of DDW as was used in the previously reported pH experiment - refer to section 2.3.2). The mixture was then then subjected to agitation by a mechanical shaker (IKA LABORTECHNIK, HS250 basic) at 180 osc min⁻¹ for a period of 15 min. A 10 ml aliquot of the filtered solution was analysed by inductively coupled plasma mass spectrometry (ICP-MS) to measure the level of major and trace elements that had been leached to water.

The levels of aluminium, cadmium, chromium, copper, lead, magnesium, manganese, nickel, and zinc released into distilled deionised water (DDW) as a result of contact with the Blueguard® materials were all below the limits of detection (Table 2-7). The levels of calcium, potassium, magnesium and sodium are as shown in Table 2-9. These levels are typical of those found for natural waters (Al-Khashman, 2009) and therefore Blueguard® solids should be a suitable wastewater treatment option. Blueguard® G1-3 and Blueguard® G1-3C not only contain higher levels of calcium (as XRF data revealed in Table 2-2) but also these materials release higher levels of calcium to water compared to the powder form of the Blueguard® materials. As mentioned in section 2.3, this is due to calcium-containing binders, which have been used to alter Blueguard® 63 to a granular form.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blueguard® 63</td>
<td>2153</td>
<td>1961</td>
<td>259</td>
<td>1324</td>
</tr>
<tr>
<td>Blueguard® G1-3</td>
<td>1000</td>
<td>18</td>
<td>37</td>
<td>25967</td>
</tr>
<tr>
<td>Blueguard® G1-3C</td>
<td>1088</td>
<td>19</td>
<td>53</td>
<td>25606</td>
</tr>
</tbody>
</table>

### 2.8 Summary

Various techniques were used to evaluate the physical and chemical properties of the three Blueguard® materials under investigation as potential remediation materials for water treatment. X-ray fluorescence spectrometry (XRF) was used for the determination of elements/compounds that exist in Blueguard® materials (refer to Table 2-2). Based on this technique SiO₂, MgO, Al₂O₃ and CaO are the major components available in these materials. Brunauer–Emmett–Teller (BET)
analysis (refer to Figure 2-6 and Figure 2-8) revealed that Blueguard® materials are non-porous with weak adsorbent-adsorbate interactions. X-ray Diffraction (XRD) was employed to characterise and confirm the main compounds present in the Blueguard® materials (refer to Table 2-3). XRD analysis showed that the main compounds in Blueguard® materials are alteration products of Mg-rich silicates namely olivine, talc, clinochlore, antigorite, biotite and ferroactinolite.

Inductively coupled plasma mass spectrometry (ICP-MS), the main analytical technique for this research (refer to section 2.7), was applied to measure the level of major and trace elements in the water samples, pre- and post-contact with the Blueguard® materials. The results confirmed that all three Blueguard® materials (powder or granular) are not a threat to the environment as they do not release any harmful compounds or elements when applied to water (with all trace element levels below the limit of detection, typically <0.1 µg l⁻¹, and major elements at levels typically found for natural waters (refer to Table 2-9).

After a set of characterisation methods and analysis described in this chapter, the applicability of these materials in wastewater remediation will be discussed in the following chapters. Two different types of contaminated water and the application of the Blueguard® materials in remediating these have been studied in this research (later Chapters). One source was stormwater contamination due to motorway pollution (section 3.3) and the other was lagoons contaminated as a result of industrial discharge (Chapter 4).
Chapter 3 Performance of Blueguard® on Contaminated Water

In this chapter, the methodology used for the analysis of contaminated water, with a focus on the level of contamination due to trace elements, is described. Samples for this purpose are mainly relevant to motorway-linked pollution, as surface runoff or stormwater is regarded as a major source of water-borne chemical release into the adjacent environment (especially drainage systems leading to local stormwater ponds and streams or rivers) (see Chapter 1).

The application of Blueguard® materials, namely, Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C (refer to section 2.2), using simulated motorway stormwater is presented in this chapter. The synthetic solutions consisted of three types (i) a multi-element (Cd, Cr, Cu, Fe, Pb, Mn, Ni and Zn) solution prepared from analytical standards (used to evaluate the trace element removal efficiency of the materials under different pH conditions); (ii) motorway dust mixed with university lake water (to evaluate the application of the materials using ‘naturally-contaminated’ water in contact with motorway dust); and (iii) digested London Orbital M25 motorway dust mixed with rainwater. This last solution was prepared from acid digested M25 motorway dust (collected in 1999 from the hard shoulder between junctions 5 and 6) which was mixed with rainwater collected from the University of Surrey car park 4 tarmac surface; the resultant mixture provided stormwater resembling that being discharged from a major motorway, like the London Orbital M25 (Pitcher, 2002; Hares, 2000). These solutions enabled a series of experiments to be undertaken to evaluate the applicability of Blueguard® materials for the ‘chemical clean-up’ of motorway stormwater, in terms of dose (mass of material per unit volume of solution) and contact time (batch equilibrium mixing time of material with the solution) under specified pH conditions.

3.1 Adsorption / Desorption (batch equilibrium)

Removing trace elements from the contaminated water was carried out using a batch equilibrium method, also known as a static system. In this method a certain mass of solid material is added to the contaminated solution with a known solid / liquid (S/L) ratio in order to see the adsorption/desorption effect. The mixture is then shaken for a specific period of time and the reduction of the contaminants in the solution is monitored using analytical techniques (Wang et al., 2009). The
benefit of the batch approach is that all variables of interest can be obtained experimentally without requiring much space for experiment apparatus. This approach is considered the quickest and simplest experimental procedure by which contaminants can be removed from the solution. However, the batch approach is criticised because the S/L ratio is often different from that observed in the field (Wang et al., 2009).

To avoid the potential costs and for more realism in use, Blueguard® was not pre-treated (washed or modified).

Quantities of different types of Blueguard® materials were weighed into polypropylene bottles to which the homogenised and filtered contaminated water was then added. Samples were shaken and filtered immediately. An aliquot of filtered solution was stored in polypropylene bottles at 4°C until analysis by inductively coupled plasma mass spectrometry (ICP-MS) which was discussed in section 2.7.

3.2 Removal Efficiency of Blueguard® under Controlled Conditions

Here a set of experiments was carried out in order to understand the effect of pH and that of the Blueguard® materials. In summary, the experiments evaluated the effect of:

a. pH on trace element levels in a multi-element solution;
b. Blueguard® materials on pH in DDW and a multi-element solution; and
c. Blueguard® materials on trace element levels in a multi-element solution.

It is important to state that these separate experiments were designed to evaluate whether the possible removal of a trace element was due to a pH effect following the addition of the Blueguard® materials or as a result of the chemistry of the Blueguard® material itself.

As mentioned in section 1.3.5, knowing the limit of solubility is important as the formation of solid particles may take place above this limit. Table 3-1 shows the pH at which various trace elements precipitate as metal hydroxides. These data will then be compared against the findings of the experiments in this section.
Table 3-1 Major species and the pH of saturated solutions of freshly precipitated metal hydroxides, and the solubility products of hydroxides pKs (Orlov et al., 2013)

<table>
<thead>
<tr>
<th>Oxidation state of the metal in a hydroxide</th>
<th>Molecular form in the saturated state</th>
<th>pH</th>
<th>pKs= –logKs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al^{3+}</td>
<td>Al(OH)_3</td>
<td>7.15</td>
<td>33.0</td>
</tr>
<tr>
<td>Cd^{2+}</td>
<td>Cd(OH)_2</td>
<td>9.37</td>
<td>14.3</td>
</tr>
<tr>
<td>Cr^{3+}</td>
<td>Cr(OH)_3</td>
<td>8.05</td>
<td>30.2</td>
</tr>
<tr>
<td>Cu^{2+}</td>
<td>Cu(OH)_2</td>
<td>7.71</td>
<td>19.3</td>
</tr>
<tr>
<td>Fe^{2+}</td>
<td>Fe(OH)_2</td>
<td>9.17</td>
<td>15.2</td>
</tr>
<tr>
<td>Fe^{3+}</td>
<td>Fe(OH)_3</td>
<td>7.00</td>
<td>38.6</td>
</tr>
<tr>
<td>Mn^{2+}</td>
<td>Mn(OH)_2</td>
<td>9.85</td>
<td>12.7</td>
</tr>
<tr>
<td>Ni^{2+}</td>
<td>Ni(OH)_2</td>
<td>9.23</td>
<td>14.7</td>
</tr>
<tr>
<td>Pb^{2+}</td>
<td>Pb(OH)_2</td>
<td>10.0</td>
<td>15.1</td>
</tr>
<tr>
<td>Zn^{2+}</td>
<td>Zn(OH)_2</td>
<td>8.97</td>
<td>15.6</td>
</tr>
</tbody>
</table>

3.2.1 Effect of pH on trace element levels in a multi-element solution

This preliminary experiment investigated the effect of pH on the solubility/precipitation of various trace elements in a multi-element solution. A 1000 µg l\(^{-1}\) multi-element solution (MES) (containing Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn) was prepared from commercial stock solutions (1000 mg l\(^{-1}\)) and the pH adjusted to 2.3, 3, 4, 5, 6, 7, 8 and 9 (using (NaOH(aq) (0.1 mol dm\(^{-3}\), trace element grade, Fisher Scientific, UK) and 1% HNO\(_3\) (Trace analysis grade, Fisher Scientific, UK). The resultant solutions were then analysed by ICP-MS (refer to section 2.7), and comparisons made between the effect of changing pH 2.3 through to 9 (see Equation 8).

\[
\frac{L_{pH2} - L_{pHx}}{L_{pH2}} \times 100\% \\
\text{Equation 8}
\]

where; ‘L’ is the level of trace element in the solution in µg l\(^{-1}\) and ‘x’ is the pH value (2.3 to 9).

Figure 3-1 and Figure 3-2 shows the results for all of the elements studied over the pH range of 2.3 to 9.

**Aluminium**

Figure 3-1 shows the trend for aluminium. Clearly, there is an increase in the precipitation of aluminium with increasing level of pH.
For pH 3, 4 no precipitation occurred, at pH 5 and 6 there was 28.1% and 34% precipitation, respectively. However, increasing the pH to 7, 8 and 9 resulted in 74.5%, 83.6% and 85.5% precipitation, respectively. This aligns with Table 3-1, where precipitation of aluminium hydroxides occurs at a pH value of 7.17 (Orlov et al., 2013).

**Cadmium**

Figure 3-2 (a) shows the trend for cadmium and that the precipitation of this element from the multi trace element solution improved as the pH increased. For pH 3, 4, 5 and 6 less than 15% of this element was precipitated; however, increasing the pH to 7, 8 and 9 resulted in 41%, 61% and 77% precipitation from this element from the solution, respectively. These findings agree with Table 3-1 which suggests precipitation of cadmium hydroxides occurs at a pH value of 9.37 (Orlov et al., 2013). Further removal of cadmium and the other trace elements discussed here using Blueguard® materials as well as the effect of these materials on pH of the solution (MES) was then studied and the results are presented in sections 3.2.2 and 3.2.3, respectively.
Figure 3-2 Effect of pH on the % removal of (a) Cd, (b) Cu, (c) Cr, (d) Fe, (e) Mn, (f) Ni, (g) Pb and (h) Zn from a multi-element solution, MES
**Chromium**

Similar to cadmium, for pH 3 and 4 less than 15% of chromium was precipitated (Figure 3-2 (c)), however around 40% of this element precipitated when the pH increased to 5 and 6. As pH increased further to 7, 8 and 9 the precipitation was enhanced to 77%, 87% and 92%, respectively. These results are supported by literature data where a study on heavy metal removal reported that, Cr(III) was precipitated when the pH value is 7 with a minimal solubility of 0.04 mg l\(^{-1}\) (Wang *et al.*, 2004). Orlov *et al.*, (2013) reported that the precipitation of chromium hydroxide occurred at a pH value of 8.05.

**Copper**

Based on Table 3-1 precipitation of copper hydroxides occurs at a pH value of 7.71 (Orlov *et al.*, 2013). Figure 3-2 (b) shows around 35% precipitation of copper at pH values of 3, 4 and 5. The level of precipitation was further enhanced to 52%, 84% and 95% when the pH of the solution was increased to 7, 8 and 9, respectively. This is in line with the findings in this study as 84% of dissolved copper in MES solution was removed at a pH value of 7.

**Iron**

Iron showed a slight difference in the pH effect on precipitation compared to other elements investigated in this study. This may be due to iron having different speciation and solubility behaviour. Precipitation of iron at pH values of 3, 4, and 5 were 12%, 18% and 56%, respectively (Figure 3-2 (d)). As reported in Table 3-1, iron has a low solubility at pH values of 7.00 and 9.17 depending on the related species. The results in, Figure 3-2 (d), showed that at pH 7 there was a 77% precipitation of iron, which confirms the findings provided by Orlov *et al.*, 2013.

**Lead**

As with all of the other trends lead precipitation increased as the pH value of the solution was incremented. The data (Figure 3-2 (g)) shows that precipitation below pH 5 was less than 16%, however 65%, 46%, 81%, 90% and 93% precipitation occurred at pH 5, 6, 7, 8 and 9, respectively. These findings are not in line with Hem (1976) who suggested that lead is very soluble below a pH value of 8.
**Manganese**

Precipitation of Mn as a result of an increase in pH was not as successful as only around 10% was precipitated between the range of pH 3 to 7, Figure 3-2 (e). This value improved slightly to 24% and 34% as the pH increased to 8 and 9, respectively. This could be due to the fact that for manganese, the optimum pH for precipitation as Mn(OH)$_2$ is between 11.5 and 12.5. The reason for such a high pH value for complete precipitation of manganese is the formation of complex ions (Sincero & Sincero, 2002). As reported in Table 3-1 (Orlov et al., 2013) manganese has a low solubility at a pH value of 9.85. Therefore, in the subsequent experiments (section 4.3) the effect of further increase in the level of pH (i.e. 10) on precipitation of this element is explored.

**Nickel**

Nickel precipitation was low, less than 30%, until the pH value increased to levels of 8 (62%) and 9 (88%), Figure 3-2 (f). This trend is in agreement with the data in Table 3-1 suggesting that nickel hydroxide is produced at a pH value of 9.23 (Orlov et al., 2013). The nickel and cadmium precipitation trends are very similar to each other, this can be related to similar solubility products of these two elements as shown in Table 3-1. One study reported that adjusting the pH level to 7.5 and 10.5 caused 71% and 85% precipitation of Ni (II), due to the formation of insoluble hydroxide compounds with increasing pH (Kurniawan et al., 2006).

**Zinc**

Figure 3-2 (h) shows the results for zinc, which are similar to those of cadmium (Figure 3-2 (a)) in that there was minimal precipitation at pH 3 to 6, around 15%. This can be related to their close It is not until the pH of the solution was increased to 7 where 46% of zinc precipitation took place. Finally, by increasing the pH to 8 and 9 precipitation improved to 78% and 90%, respectively. Kursunoglu and Kaya (2013) used NaOH as a precipitating agent to precipitate dissolved Zn in solution. They showed 99.99% of Zn is removed at a pH value of 8. Based on the findings presented by Orlov et al., (2013) full precipitation of zinc hydroxides occurred at a pH value of 8.97.

The data presented in this experiment show, that the precipitation of trace elements occurs with increasing pH. Moreover, enhanced precipitation occurs
above a pH level of 7. In general, the data is in agreement with other published results.

### 3.2.2 Effect of Blueguard® on pH in DDW and a multi-element solution

Before studying the effect of Blueguard® materials on the removal of trace elements from the multi-element solution (MES), an experiment was undertaken to evaluate any impact the addition of the materials may have on the pH of a solution was carried out. The reason for this is that there is evidence to suggest that the dispersion may also cause a change in the chemistry of water and subsequently result in pH variation. Therefore, 50 ml of distilled water and the MES were prepared at different pH values of 2, 7 and 9. To each solution was added 0.5 g Blueguard® 63, G1-3 or G1-3C and the pH values of these mixtures were measured using a calibrated pH meter. The results are presented in Table 3-2.

<table>
<thead>
<tr>
<th>Materials</th>
<th>DDW</th>
<th>MES solution</th>
<th>pH adjusted MES solution</th>
<th>pH adjusted MES solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (blank)</td>
<td>6</td>
<td>2</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>Blueguard® 63</td>
<td>9.9</td>
<td>2.1</td>
<td>8.3</td>
<td>9.4</td>
</tr>
<tr>
<td>Blueguard® G1-3</td>
<td>9.9</td>
<td>2.0</td>
<td>8.3</td>
<td>9.3</td>
</tr>
<tr>
<td>Blueguard® G1-3C</td>
<td>9.9</td>
<td>2.0</td>
<td>8.3</td>
<td>9.3</td>
</tr>
</tbody>
</table>

The data showed that the pH difference of the MES solution before and after addition of the materials is the same for Blueguard® G1-3 and Blueguard® G1-3C under acidic condition (pH 2). The pH value of the MES solution increased by 0.1 after the addition of Blueguard® 63 under acidic conditions. In contrast, there is a big impact on the pH level of de-ionised water (DDW), increasing the pH value from 6 to ca. 10. This may be due to the release of hydroxide ions (OH⁻) from the materials. Therefore, hydroxide release due to Blueguard® materials resulted in a substantial increase of pH of DDW. However, this effect is too small to influence the acidity of the MES solution. Following the adjustment of the pH level of the MES solution, the addition of the Blueguard® materials raises the pH from 7 to 8.3 and from 9 to 9.4. Therefore, in summary, this material has shown a benefit of removing trace elements while not substantially increasing the pH level of a
solution that would reflect the normal pH levels of typical surface or ground waters. This is important, as any remediation technology that would result in a large pH change would be detrimental to the environment, especially ecosystems.

3.2.3 Effect of Blueguard® on trace element levels in a multi-element solution

Having studied the pH effect, a final investigation was undertaken using MES solutions to evaluate the applicability of Blueguard® materials in removing the selected trace elements under investigation. It should be stressed that the MES solution was prepared with those elements that have been found to be raised in motorway stormwater (Legret & Pagotto, 2006; Barbosa & Hvitved-Jacobsen, 1999). This was investigated by batch equilibrium involving 50 ml of MES solution mixed with 0.5 g of each of the three types of Blueguard® (in duplicate) and shaken for 5, 15 and 30 min (contact times). This was carried out at each initial pH level under investigation: 3, 4, 5, 6, 7, 8 and 9 (see Equation 9).

The data are presented as a percentage (%) precipitation, using the following calculation method for each of the experiments:

\[
\frac{L_{MES\text{only}} - L_{Blueguard}}{L_{MES\text{only}}} \times 100\% \quad \text{Equation 9}
\]

where; ‘\(L\)’ is the level of trace element in the solution in µg l\(^{-1}\), ‘\(L_{MES\text{only}}\)’ and ‘\(L_{Blueguard}\)’ is the solution before and after adding Blueguard® materials, respectively.

This experiment evaluated the effect of Blueguard® on the removal of trace elements for various pH levels, the results are discussed in the following subsections by trace element. The reason no values are given for pH 2 is because there was no measurable difference in the level in trace elements; the metals are therefore not removed from solution at low pH.
Aluminium

The data in Figure 3-3, show the percentage removal of aluminium by the application of Blueguard® 63, G1-3 and G1-3C, for pH levels 3 through to 9 and at the various contact times of 5, 15 and 30 min.

Figure 3-3 Removal efficiency of aluminium by Blueguard® 63, G1-3 and G1-3C following the addition to the MES for contact times 5, 15 and 30 min. Where no error bars are visible these are within the symbol size.
After a 5 min contact time and at a pH of 4 aluminium removal from the solution was ~63%, for all Blueguard® types. This increased gradually to ~89% at pH 9.

At pH 4 and 15 and 30 min contact times the removal efficiency increased with ~88% and 97% aluminium removal, respectively. It took until pH 5 and a 15 min contact time for the removal percentage to begin to level off and remained at ~95 +/-3% removal up until pH 9. For the 30 min contact period, the levelling off effect started from pH 4 and remained at an average ~97 +/- 3% aluminium removal until pH 9. The data in this section are the average removal percentages for Blueguard® 63, G1-3 and G1-3C.

**Cadmium**

The graphs in Figure 3-4, show the percentage removal of trace element by the application of Blueguard® 63, G1-3 and G1-3C, for pH levels 3 through to 9, at the various contact times 5, 15 and 30 min.

It is clear from the graphs that as the pH level is increased so does the percentage removal of cadmium. In general, across the different contact times the trend for Blueguard® G1-3 and G1-3C follow each other. However, this is not true of Blueguard® 63, where there appears to be a shift / delay compared to the other Blueguard® types, as it takes a higher pH level to remove the cadmium. This delay could be due to the fact that Blueguard® 63 a fine powder (refer to section 2.2) when compared with the more granular forms of the other two types of the Blueguard® materials. Therefore, with the increased surface area of this material it behaves differently with regards to the cadmium ions in solution.

At 5 min contact time the Blueguard® materials were not efficient at pH 3 and 4. However, Blueguard® 63, G1-3 and G1-3C managed to remove 18.5%, 70% and 80% of cadmium in the multi trace element solution at pH 5, respectively. This trend improved as the pH increased, at pH 8 97%, 95% and 97% removal occurred for Blueguard® 63, G1-3 and G1-3C, respectively.
Figure 3-4 Removal efficiency of cadmium by Blueguard® 63, G1-3 and G1-3C following the addition to the MES for contact times 5, 15 and 30 min. Where no error bars are visible these are within the symbol size.
Increasing the contact time to 15 min resulted in 8%, 80% and 96% removal efficiency at pH 4. This is a vast improvement compared to the 5 min contact time, approximately 2x, 40x and 9.6x for Blueguard® 63, G1-3 and G1-3C, respectively. This difference is attributed to the longer contact period. At pH 7 approximately 98% of the material was removed for all Blueguard® types, this occurring one pH level lower than for the 5 min contact period.

For the longest contact time of 30 min at pH 4 removal of 81%, 99% and 99% occurred for Blueguard® 63, G1-3 and G1-3C, respectively. This follows the difference seen between the lower contact times, whereby increasing the contact time more cadmium is removed for a lower pH level. At a pH of 7 Blueguard® 63 caught up with the other two by achieving 99% removal of cadmium.

When comparing the results with section 3.2.1 (Figure 3-2 (a)), it is evident that all of the Blueguard® types have a positive impact on the MES, by removing more of the cadmium from the solution. At pH 5 and 5 min contact time, 12%, 19%, 70% and 80% of the cadmium was removed for no Blueguard®, then Blueguard® 63, G1-3 and G1-3C, respectively. This shows a 6.7x increase between purely the effect of pH and that of applying Blueguard® G1-3C, at 30 min contact time this factor is 8.3x. Similarly, at pH 9, only 77% of cadmium is removed due to pH, however for all Blueguard® material types approximately 96% of the cadmium is removed. This further reduction can be attributed to the additional increase of pH (Table 3-2) and further precipitation.

This experiment showed that Blueguard® G1-3C in general was the best option compared to the other two materials in removing cadmium from the solution.

**Chromium**

In Figure 3-8 the results for chromium are shown for all Blueguard® types, contact times and pH values. Compared with cadmium, the removal efficiency of chromium by all Blueguard® materials was higher, with more removal happening at a lower pH. At 5 min contact time and a pH of 4 75 to 87% of chromium was removed from the solution. However, as a comparison under these experimental conditions only 4 to 8% of cadmium was removed, for all Blueguard® types.
Figure 3-5 Removal efficiency of chromium by Blueguard® 63, G1-3 and G1-3C following the addition to the MES for contact times 5, 15 and 30 min. Where no error bars are visible these are within the symbol size.
In terms of the different contact times, at 5 min for Blueguard® G1-3C ~87% of chromium was removed, whereas for 15 and 30 min contact times 98% and 99% removal occurred, respectively. It took until pH 7 for ~98% removal of chromium for all Blueguard® types at 5 min contact time.

In general, the trend show that by increasing pH the % removal of chromium increases, and for a higher contact period more removal happens at a lower pH. At a pH of 4 and 5 min contact time, 87% chromium removal occurs for Blueguard® G1-3C to ~98% and 99% for 15 and 30 min contact times, respectively. Although the trend for all Blueguard® materials are similar, Blueguard® G1-3C is seen to perform slightly better at the lower contact times, with ~0 to 5% more removal compared to Blueguard® 63 and G1-3.

There is also a noticeable improvement between the results as shown in Figure 3-2 (c) and Figure 3-5, with up to 87% chromium removal at pH 4 for all Blueguard® materials and 5 min contact time, compared with 14% precipitation with no Blueguard®.

**Copper**

The removal patterns for copper are quite similar to those for chromium, as shown in Figure 3-6. Despite the minimal removal of copper (< 12%) by the Blueguard® materials at pH 4 for all contact times, the efficiency improved to 74%, 86% and 78% at pH 5 for Blueguard® 63, G1-3 and G1-3C at 5 min contact time, respectively. The efficiency improved to a maximum 98% and 100% at pH 7, 8 and 9 respectively, for the same contact period. Increasing the pH level of the multi element solution to pH 5 with a contact time of 15 min was sufficient to remove 99% of copper for all Blueguard® materials. This occurred at a lower pH level of 4 with a 30 min contact time.

Compared with Figure 3-2 (b), where no Blueguard® was used, at pH 5 only 38% of the copper was removed, whereas with Blueguard® even at 5 min contact time at least 70% of the copper was removed from the solution.
Figure 3-6 Removal efficiency of copper by Blueguard® 63, G1-3 and G1-3C following the addition to the MES for contact times 5, 15 and 30 min. Where no error bars are visible these are within the symbol size.
The trend for iron at 5 min contact time is similar to that of cadmium, with Blueguard® 63 lagging behind the removal efficiency of Blueguard® G1-3 and G1-3C, as shown in Figure 3-7.

![Removal efficiency of iron by Blueguard® 63, G1-3 and G1-3C following the addition to the MES for contact times 5, 15 and 30 min. Where no error bars are visible these are within the symbol size.](image_url)
Again, this lag can be attributed to the blending or mixing of the fine particles of the Blueguard® 63 with the MES, as had been noticed with some of the other trace element removal (< 18%) occurred at pH 3. At pH 4 and a contact period of 5 min, 7%, 50% and 92% removal of iron occurred for Blueguard® 63, G1-3 and G1-3C, respectively. This increased to 59%, 96% and 96% for Blueguard® 63, G1-3 and G1-3C, respectively, at pH 5. Furthermore, at pH 7 the removal efficiency of iron reached ~96% for all Blueguard® types.

At pH 4, increasing the contact times to 15 and 30 min resulted in the removal of 90% to 99% of the iron for all Blueguard® types. This increased to 98% for all materials at pH 5. In terms of comparing the data with the pH only study and no Blueguard®, as shown in Figure 3-2 (d), only 56% of Fe was removed from the MES (pH 5).

**Lead**

The removal of lead showed the most promising data, as reported in Figure 3-8. Lead removal from the multi element solution using all Blueguard® materials was the most successful with 92% to 100% removal at pH 4 for all contact times. This is compared with 4% to 37% removal at pH 3 for all contact times and Blueguard® types. The potential of these materials to remove lead is also highlighted by comparing the data with the results in Figure 3-2 (g), where no Blueguard® material was used with only 7% and 16% lead removed at pH 3 and 4, respectively.

There is also a negligible difference in the removal efficiency of lead between the different Blueguard® materials after pH 4. Interestingly, at pH 3 Blueguard® G1-3C has a slightly better performance with ~21% removal of lead for a 15 min contact time, compared with 6% and 15% for Blueguard® 63 and G1-3, respectively.
Figure 3-8 Removal efficiency of lead by Blueguard® 63, G1-3 and G1-3C following the addition to the MES for contact times 5, 15 and 30 min. Where no error bars are visible these are within the symbol size.

Manganese
In contrast to lead, manganese showed the worst performance overall, as seen in Figure 3-9. After a 5 min contact time, the removal efficiency of the Blueguard® materials removal efficiency incremented gradually for the different pH values of 3, 4, 5, 6, 7 and 8. The maximum removal of manganese of 92%, 97% and 97% occurred for Blueguard® 63, G1-3 and G1-3C, respectively, at pH 9. It is notable that a similar weak trend was observed in the study where no Blueguard® was used, as shown in Figure 3-2 (e). At pH 9 only 34% removal of manganese was observed in the pH only study (refer to section 3.2.1).

This removal efficiency trend was improved by increasing the contact time to 15 min. Results show that a 46%, 80% and 85% removal of manganese took place at pH 5 for Blueguard® 66, G1-3 and G1-3C, respectively. In contrast, Blueguard® G1-3 and G1-3C begin to flatten-off above pH 6 with a ~98% removal of manganese and for Blueguard® 66 a level of ~53% removal.

Increasing the contact time further had a positive effect from pH 4 for Blueguard® G1-3 and G1-3C beginning to level off with ~93% and ~98% manganese removal, respectively. However, it still took till pH 7 for Blueguard® 66 with a ~94% removal efficiency of manganese.

Again this compares with the trend seen in Figure 3-2 (e). However, in this case Blueguard® materials have a positive removal effect, with Blueguard® G1-3C at a 30 min contact time, showing a 12.3x improvement at pH 4.
Figure 3-9 Removal efficiency of manganese by Blueguard® 63, G1-3 and G1-3C following the addition to the MES for contact times 5, 15 and 30 min. Where no error bars are visible these are within the symbol size.
**Nickel**

Figure 3-10 shows the results for nickel for all Blueguard® materials, pH levels and contact times.

![Graph showing nickel removal efficiency](image)

*Figure 3-10 Removal efficiency of nickel by Blueguard® 63, G1-3 and G1-3C following the addition to the MES for contact times 5, 15 and 30 min. Where no error bars are visible these are within the symbol size*
The results for nickel (Figure 3-10) compare well with those for cadmium (Figure 3-4), in that the trends are similar, even for the graphs in the pH only study (Figure 3-2 (a) and (f)).

With the 5 min contact period it took until pH 7 for Blueguard® G1-3 and G1-3C to begin levelling off, and Blueguard® 66 from pH 8. At pH 9 the 92%, 96% and 96% for Blueguard® 66, G1-3 and G1-3C, respectively.

With a higher contact period of 15 min the results shifted to the left, meaning that more removal occurred at a lower pH. For example, at pH 6, 47%, 99% and 99% removal of nickel for Blueguard® 66, G1-3 and G1-3C, respectively. Blueguard® 66 begun to peak at pH 7 with ~94% removal of nickel.

At the highest contact time of 30 min and a pH of 4 the respective removal levels of nickel were 55%, 99% and 99% using Blueguard® 63, G1-3 and G1-3C. However, like with the 15 min contact time Blueguard® 66 only begun to level off at pH 7 with ~99% removal of nickel. Comparing these results with those from the pH only study (refer to section 3.2.1), at pH 4 only 14% of the nickel was removed from solution.

As with the previous results Blueguard® G1-3C tends to show a general better performance for elemental removal. This is clearly seen at a 15 min contact time, and a pH 4 resulting in ~91.5% removal of nickel, compared with only ~5.5% and ~65% for Blueguard® 63 and G1-3, respectively. A lower removal efficiency of Blueguard 63 was observed for this element as well.

**Zinc**

Zinc removal appears has shown to be more efficient at a contact time of 30 min, which is similar to the data for the previous trace elements. These results are shown in Figure 3-11.

As reported for cadmium, iron, manganese and nickel there is a gradual upwards trend from pH 3 to 9 in removal percentage of zinc, at a 5 min contact time. At pH 5 the removal of zinc increased to 49%, 70% and 82% when applying Blueguard® 63, G1-3 and G1-3C, respectively. This finally reached above ~95% zinc removal at pH 7.
Figure 3-11 Removal efficiency of zinc by Blueguard® 63, G1-3 and G1-3C following the addition to the MES for contact times 5, 15 and 30 min. Where no error bars are visible these are within the symbol size.
Increasing the contact time to 15 min improved the removal efficiency at pH 4 for Blueguard® G1-3 and G1-3C with 92% and 97% removal of zinc, respectively; while using Blueguard® 63 only ~19% of zinc was observed. Blueguard® 63 caught up with the other materials at pH 6, with all at around 96% to 99% removal of zinc. The removal efficiency of all the Blueguard® materials was above 95% at pH 4 for a contact time of 30 min. This levelled off for the subsequent pH levels.

In general, Blueguard® 63 was shown to be the more efficient at removing zinc when compared with Blueguard® G1-3 and G1-3C. Increasing the contact period minimised this difference.

In contrast to the pH only experiment, the results at pH 7 shown in Figure 3-2 (h), resulted in ~46% of the zinc being removed from solution. In contrast with the application of all Blueguard® materials and at all contact times, the zinc removal was above 95%.

One reason for the good removal efficiency of zinc at pH 7 in terms of the application of Blueguard® materials can be due to the effect on the pH of the multi-element solution (MES). As shown in Table 3-2, adding Blueguard® materials to MES at a pH value of 7, increases the pH of this solution to 8.3. This is close to the value of 8.97 (from Table 3-1) which Kursunoglu and Kaya (2013) suggested would result in the precipitation of zinc from solution.

The above experiments were all undertaken using the batch equilibrium method. However, in terms of exploring the possible ‘field-based’ methodologies of using these materials to remediate contaminated waters, it was considered important to evaluate the trace element removal efficiency under column experimental conditions.

3.2.4 Column test study of effect of Blueguard® G1-3 on trace element levels in a multi-element solution

A laboratory column study was chosen as the second step of studying the removal efficiency of Blueguard® materials in contact with a multi-element solution (MES). The main purpose of this part of the experimental study was to investigate the materials effectiveness in removing the trace elements under the
dynamic system as well as gaining an insight into the exhaustion point of the materials.

Following an evaluation of the batch equilibrium results it was decided to only use the Blueguard® G1-3 material for the column experiments. As the ultimate purpose of this research is the application of Blueguard® materials on natural wastewater treatment (at a typical pH of 7), the MES solution was adjusted to 7 pH. The solution was then fed through the column containing 0.50 g of the material, providing a fixed head of solution on the top of the packed material. A constant flow rate of the MES (pH 7, 50 ml) was applied at the top of the column and 45 fractions were collected. The levels of Al, Cr, Cd, Fe, Mn, Ni, Pb and Zn were then determined using ICP-MS and the results are shown in Figure 3-12. Here the percentage of removal versus fraction is provided for each of the trace elements under study in the MES solution.

As shown in Figure 3-12, a percentage removal of all elements occurred after the initial fraction. Various trace elements including Cu, Cd, Mn, Ni and Pb were completely removed (100% removal efficiency) after the first pass of the MES solution through the column. However, for Fe and Zn, 86% and 87% removal took place, respectively. The slightly reduced levels of removal of Fe and Zn compared to the other elements, especially when there is competition among various elements, may be attributed to their smaller solubility product constants (refer to section 1.3.5). A further 45 volumes (of 50 ml) of the MES solution were passed through the column and the Blueguard® G1-3 material remained effective in removing the various trace elements from the solution. This implies that the material has a very large affinity to remove trace elements. This will be evaluated in further experiments. Aluminium results, however, were not as good as the other trace elements, with only 55% removal for the first fraction, increasing to 90% at fraction 10, then levelling off for the subsequent fractions to an average of 88.9% +/-10%.
3.2.5 Summary

In most of the experiments, increasing the pH value of the multi trace element solution (MES) to 7 resulted in the removal of various trace elements, including chromium (77%), copper (84%), iron (77%) and lead (81%). However, increasing
the pH of the MES to a value of 7 did not result in the enhanced removal of cadmium (41%), manganese (9%), nickel (28%) and zinc (46%). With the application of Blueguard® materials a further reduction of these elements was observed, namely for zinc, where up to a 99% reduction in the level of dissolved zinc occurred for the same pH level. This shows that the reduction in the level of trace elements is not just due to a change in initial pH but also to the effect of the Blueguard® materials.

Increasing the pH of the multi-element solution (MES) to 9 resulted in the removal of trace elements ranging from 34% (for manganese) up to 93% (for lead) as shown in Figure 3-2 (e) and (g), respectively. Interestingly, the level of trace elements reduced from the MES after further application of Blueguard® materials. The best reduction occurred at pH 9 resulting in a 66% removal of manganese as shown in Figure 3-9.

It was also noticeable from the results in section 3.2.3 that the longer contact time resulted in increased trace element removal from the MES at lower pH levels.

These results clearly show that Blueguard® materials have applicability in remediating the level of pollutant trace elements in the solution under neutral or alkaline conditions. Blueguard® materials, however, could not remediate multi-trace elements in the solution under acidic conditions (especially at pH 2). It is also assumed that the mechanism, by which Blueguard® materials’ remove trace elements from the solution is by precipitation, as these materials release hydroxide ions to the solution that result in the formation and precipitation of elemental / metal hydroxides. This hypothesis will be further investigated in the following chapter, in which Blueguard® materials will be further characterised, using the techniques discussed in Chapter 2, after contact with a contaminated solution that was chemically prepared to represent an industrial discharge wastewater.

As the MES solution was originally acidic (as a result of the dilution of commercial elemental stock solutions in the laboratory – each element is stabilised being stored in nitric acid), further investigations were undertaken using natural environmental samples. The results are discussed in the following sections as well as in the next chapter.
3.3 Treating a Motorway-related Contaminated Solution with Blueguard® 63

The next preliminary pilot study was designed to evaluate Blueguard®63 under batch equilibrium conditions using University of Surrey lake water mixed with motorway dust (collected from the M25, Oxted in 1999). Different masses of Blueguard®63 (0.25 to 0.75 g) and contact times (2 to 120 min) were used to reach the optimised conditions for the removal of trace elements from the solution.

University of Surrey lake water or UoS LW was collected in May 2012, using 1 litre plastic containers which were prewashed with water from the same source. Motorway dust collected from the M25 (Oxted 1999) was added to the UoS LW samples (modif-UoS LW) and then subjected to mixing by a mechanical shaker (IKA LABORTECHNIK, HS250 basic) at 180 oscillations per min (osc min⁻¹) for a period of five days.

An aliquot of filtered (<0.45µm) modif-UoS LW (50 ml) was added to separate polypropylene bottles containing 0, 0.25, 0.50 and 0.75 g of Blueguard® 63 (provided by Sibelco UK Ltd.). Each solution was mixed using the mechanical shaker for different contact times.

Each mass of Blueguard® 63 was placed into 6 bottles (one for each contact time), each having 50 ml of motorway dust mixed with UoS LW or modif-UoS LW, for the batch equilibrium experiment. Each bottle was then subjected to a different contact time of 2, 5, 10, 30, 60 and 120 min. After the respective contact time, each bottle was removed, immediately centrifuged at 3000 rpm for 15 min, and a 10 ml aliquot of filtered solution was stored in polypropylene at 4 ºC until analysis by inductively coupled plasma mass spectrometry (ICP-MS). This analytical technique was used to determine the levels of Cu, Fe, Mn, Ni, Pb, and Zn for each sample (refer to section 2.7).

3.3.1 Results and discussion

The initial level of trace elements in modif-UoS LW as determined by ICP-MS are shown in Table 3-3. The results show that this modified mixture contained trace levels of Cu, Fe, Mn, Zn, Ni and Pb. Although all trace elements were below the allowable levels of the United States Environmental Protection Agency (EPA), World Health Organisation (WHO) Guidelines and UK Statutory Instruments...
(UKS1) for Drinking Water Quality (section 1.2), contact with Blueguard® 63 resulted in a significant reduction of the elemental levels within a contact time of 5 min.

Table 3-3 Trace element levels (µg l⁻¹) in University of Surrey lake water mixed with motorway dust

<table>
<thead>
<tr>
<th>Element (µg l⁻¹)</th>
<th>Cu</th>
<th>Fe</th>
<th>Pb</th>
<th>Mn</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>UoS LW</td>
<td>20.0</td>
<td>65.0</td>
<td>1.7</td>
<td>144.0</td>
<td>1.8</td>
<td>20.0</td>
</tr>
</tbody>
</table>

Figure 3-13 (a to c) and Figure 3-14 (d to f), report the levels of Cu, Fe, Pb, Mn, Ni, and Zn, respectively, for the different experimental conditions as measured using ICP-MS. Each figure provides the data as the % removal of the element as a function of contact time. The results confirm the applicability of Blueguard® 63 in wastewater treatment. However, there are some interesting variations. Iron (b), manganese (d), nickel (e) and zinc (f) show a 100% removal within a 5 min contact time. There is little difference between doses of material (namely, 0.25 to 0.75 g). In contrast, copper (a) and lead (c) show only a 60% level of removal and there is a ~10% variation due to dose (with increased mass being more effective). This may in part be due to the very low levels of these two elements in the modified lake water (modif-UoS LW). A more in-depth evaluation of the % removal of each element was undertaken using shorter contact times (typically 5 to 60 min) in an attempt to see what could result from the ‘application’ of the material in treating wastewaters (refer to section 3.4).
Figure 3-13 Percentage removal of (a) Cu, (b) Fe, (c) Pb as a function of contact time with modif-UoS LW (lake water mixed with motorway dust), following a batch equilibrium experiment with different masses of Blueguard® 63 (0.25, 0.50, 0.75)
Figure 3-14 Percentage removal of (d) Mn, (e) Ni, (f) Zn as a function of contact time with modif-UoS LW (lake water mixed with motorway dust), following a batch equilibrium experiment with different masses of Blueguard® 63 (0.25, 0.50, 0.75)
Manganese

The capability of Blueguard® 63 in removing manganese from modif-UoS LW is clearly demonstrated in Figure 3-14 (d). In general, 0.25 g of Blueguard® 63 was capable of removing 91% of the manganese present in the solution (modif-UoS LW) within a 2 min contact period. From an initial level of 144.0 µg l⁻¹ manganese, the resultant value was ~4 µg l⁻¹ manganese after 5 min of contact with the added Blueguard® 63. This result is especially outstanding as, based on the experiment carried out previously (section 3.2.1), increasing the pH of the solution to 7 resulted in only 7% precipitation of the manganese in the contaminated solution (Figure 3-2 (e)).

For the different masses of Blueguard® 63 (0.25, 0.5 and 0.75 g) the resultant manganese levels after 2 min were 13, 7 and 4 µg l⁻¹, representing an average removal of 94%. This suggests that, compared with the initial level of manganese, increasing the mass of Blueguard® 63 does not have much of an additional benefit in removing the trace element. Increasing the contact time beyond 2 min did not change the removal process either, which confirms that the process is not reversed at longer contact times. To theorise, the results suggest that the release of hydroxide ions from Blueguard® materials to the solution plays a role in the formation of insoluble hydroxide compounds with the various trace elements, for example Mn, and hence result in a decrease in the level of dissolved trace elements in the solution. Subsequent experiments in this study support this theory further (refer to 4.7).

Copper, Lead, Zinc, Iron and Nickel

After a 2 min contact period of the modif-UoS LW solution with 0.25 g Blueguard® 63, the levels of Cu, Fe, Pb and Zn were reduced by 55%, 79%, 85%, and 92%, respectively. A minimal difference in the level of Ni was observed after contact with Blueguard® 63, and can be explained by the very low initial levels of this element (1.8 µg l⁻¹ Ni).

Clearly, a 5 min contact time may not be suitable for field-based application of this material. This study also showed that modifying lake water with motorway dust was only moderately successful because some elements were at very low levels (not reflecting typical polluted wastewaters (www.8)). The next set of
experiments was extended to study all of the Blueguard® materials as remedial options (detailed in section 2.2) for treatment of water samples with higher elemental levels.

3.4 Treating Contaminated Motorway Run-off Water

As discussed in section 1.3.1, motorway run-off is one of the major sources of chemical pollution within the vicinity of transport activities. Motorway run-off is a complex mixture of rain water which contains physical and chemical components originating from transport activities (Grant et al., 2003). Motorway stormwater samples were collected from the London Orbital M25 motorway site at Oxted in October 2012 and 2013. Chemical analysis confirmed trace elemental levels to be typically of a few µg l\(^{-1}\). It was deemed that these concentrations were too low for evaluating the elemental removal efficiency of the Blueguard® materials. Therefore, to simulate motorway run-off, rainwater was mixed with motorway dust. Blueguard® materials were then evaluated as possible materials for ‘cleaning-up’ the run-off before discharge to local watercourses. The procedure in the next section describes the experimental sequence.

3.4.1 Sampling methodology for remediating motorway run-off water

After a particularly rainy week in October 2012, water samples were collected from the University of Surrey car park (UoS CPW) to provide rain water that had been subjected to traffic related pollution. All water samples were collected using 5 litre plastic containers. Motorway dust collected from the M25, Oxted (1999) was digested using concentrated nitric acid (78%) and mixed with the UoS CPW sample (modif-UoS CPW). This was carried out in order to provide a high initial level of trace elements, learning from the previous experiment (in section 3.3). The pH was then adjusted to 7, by adding aqueous sodium hydroxide (1 mol dm\(^{-3}\)), in order to simulate the conditions of ‘natural’ water.

In this experiment 50 ml of modif-UoS CPW (at pH 7), was added to 0.25 g of all three types of Blueguard® materials. The mixture was then subjected to different contact times of 5, 15, 30 and 60 min. The pH of the modif-UoS CPW solution was also measured after the addition of Blueguard® materials.
3.4.2 Results and discussion

Table 3-2 showed that mixing the Blueguard® materials with distilled deionised water (DDW) resulted in a large increase in the pH value (pH 6 to pH 9). In contrast to that experiment, addition of these materials to modif-UoS CPW (pH=7) did not influence the pH value of the solution and subsequently the pH stayed relatively unchanged (pH=7.5). This implies that the release of hydroxide ions from the Blueguard® materials in solution has resulted in the formation of insoluble metal hydroxides. This therefore limits the amount of free hydroxide ions resulting in a minimal pH change.

The initial levels of trace elements in modif-UoS CPW (at pH 7) are detailed in Table 3-4. Clearly this solution still has low levels of cadmium (1.0 µg l⁻¹ Cd) but the other elements under investigation are at higher levels than the modif-UoS LW solution used in the previous experiments.

Table 3-4 Trace element levels (µg l⁻¹) in University of Surrey contaminated car park water (modif-UoS CPW) produced by mixing car park rainwater with acid digested motorway surface dust.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>modif-UoS CPW (µg l⁻¹)</td>
<td>1.0</td>
<td>24.3</td>
<td>254.0</td>
<td>8648.3</td>
<td>914.0</td>
<td>375.0</td>
<td>64.0</td>
<td>1642.0</td>
</tr>
</tbody>
</table>

Figure 3-15 (a to d), report the levels of Cd, Cr, Cu, Fe and Figure 3-16 (e to h) report the levels for Mn, Ni, Pb and Zn, respectively, for the different experimental conditions as measured using ICP-MS. Each figure reports the data as the % removal of the element as a function of contact time. The results confirm the applicability of Blueguard® materials in projects related to remediation of stormwater contamination.
The efficiency of all three types of Blueguard® material in reducing the levels of Cd, Cr, Cu and Fe in the modif-UoS CPW solution is clearly demonstrated in Figure 3-15. Although the level of cadmium in modif-UoS CPW was initially very low (1.0 μg l⁻¹), application of Blueguard® materials could bring the level of this trace element down to around 0.16 μg l⁻¹ Cd. This showed not only the applicability of these materials in reducing the level of cadmium but also the reliability of ICP-MS to detect and monitor the level of cadmium in such waters. It also confirms that these materials are good candidates for removing cadmium from the solution as only 33% of this element would precipitate on simply adjusting the pH to 7 (refer to Figure 3-2 (a)). These materials were even more
efficient in removing high levels of iron (8648.3 µg l\(^{-1}\)). All three Blueguard\textsuperscript{®} materials removed approximately 99% of the initial iron level of the solution.

In general, as noted from earlier experiments, there is a negligible difference between the different types of Blueguard\textsuperscript{®} materials in terms of efficiency, except for the case of Cu, where Blueguard\textsuperscript{®} 63 is more efficient at removing this element (by up to 8% more removal compared to the other types of Blueguard\textsuperscript{®}).

![Figure 3-16](image1.png)

**Figure 3-16** Percentage removal of (e) Mn, (f) Ni (g) Pb and (h) Zn as a function of contact time with modif-UoS CPW (rain water mixed with digested motorway dust), following a batch equilibrium experiment using 0.25 g mass of Blueguard\textsuperscript{®} 63, G1-3 and G1-3C.

Figure 3-16 (e to h) report the % removal of Mn, Ni, Pb and Zn after applying Blueguard\textsuperscript{®} 63, G1-3 and G1-3C to the modif-UoS CPW solution. The results show 100% removal efficiency for lead using the Blueguard\textsuperscript{®} materials. Furthermore, the removal of nickel is encouraging as this element was very soluble in the experiment using a multi trace element solution at a pH value of 7.
The results in Figure 3-16 (f) clearly show Blueguard® materials could remove up to 94% of the nickel from the modif-UoS CPW solution.

As before there is little difference between the different types of Blueguard® materials in removing trace elements from modif-UoS CPW. In all of the results increasing the contact time to above 5 min does not make that much difference, suggesting that the hydroxide ions are released into the solution in a very short period of time.

3.5 Summary

This chapter focused on the remediation of contaminated motorway stormwater using Blueguard® materials, those previously introduced and characterised in Chapter 2. A set of experiments was carried out based on three types of contaminated multi trace element solutions, including (i) multi-element (Cd, Cr, Cu, Fe, Pb, Mn, Ni and Zn) solution prepared from analytical standards; (ii) motorway dust mixed with lake water; and (iii) acid digested motorway dust mixed with car park rainwater. Each of these solutions was then mixed with Blueguard® materials (Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C) and the efficiencies of these materials under different pH levels, dose and contact time were evaluated.

The results showed that olivine-containing Blueguard® materials are not applicable for trace element removal from wastewaters under acidic conditions, namely, at a pH value of 2. A suggested reason is that at this pH level, the high concentration of hydrogen ions in the solution 'neutralises' the concentration of hydroxide ions that are released from the materials. Furthermore, there is some evidence that the solids are ‘digested’ by the high acidic conditions. However, these materials were very efficient at removing various trace elements from a multi-element contaminated solution at pH values of 7 and 9. Also, a short period of contact time (less than 15 min) and a minimum dose of 0.25 g in 50 ml solution were sufficient for these materials to remove most of the trace elements from the different solutions. It is proposed, based on the chemical structure (refer to Chapter 2), that there is a possible release of hydroxide ions from the Blueguard® materials after contact with the solution. Moreover, based on the experiment using double distilled water (DDW) these materials produce a pH change to
alkaline conditions. This is possible due to an increase in hydroxide ions in solution that will result in the precipitation of insoluble metal hydroxides. This hypothesis is supported by the fact that when the materials were added to multi-element solutions (reflecting various levels of chemical contamination) there was not a significant pH change. This implies that no free hydroxide ions remain in solution, i.e. all have formed insoluble metal hydroxides, thereby reducing the trace element levels of the contaminated water.

In conclusion, this chapter focused on the use of laboratory-based experiments with ‘ideal’ solutions made to replicate possible chemically contaminated wastewaters. It is also necessary to evaluate the elemental removal efficiency of these materials under ‘real’ field-based conditions. Chapter 4 reports on research undertaken at the Cranleigh Brickworks in Surrey, a site with reported high levels of trace elements resulting from various sources, including brickworks, chemicals, and metallurgical works, etc.
Chapter 4 Industrial Discharge Treatment

This chapter evaluates the application of the Blueguard® materials (Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C) for the treatment of an industrial discharge under 'real' field-based conditions. The site is located in a rural woodland setting some two miles south of Cranleigh, Surrey (UK) and one mile north of the West Sussex county boundary. The area has an industrial history dating back almost 200 years. It is a heavily contaminated site with multiple sources of physical and chemical contaminants over the course of time. Initially, it was established as a Fuller's Earth and refractory clay works in the early 20th century. This site was chosen in 1937 by the Steetley Chemical Company as a location for chemical manufacturing operations. The chemical factory closed in 1989 and the brickworks were established just to the west of the area in 1990. This in turn closed in 2004 and the yard was used to store bricks from other factories. The site is now largely abandoned and is heavily contaminated with hazardous chemicals. An aerial view of the site is shown in Figure 4-1.

The presence of particular physical and chemical forms of contamination on the site and the associated link to Controlled Waters has led to the site being “determined” and designated a “Special Site” under the Environmental Protection Act 1990 by Waverley Borough Council (the local government authority) in 2001.

Figure 4-1 Aerial view of the Cranleigh site showing the leachate lagoon (A), middle lagoon (B) and quarry lagoon (C) (provided by Richard Armfield from Rural Arisings)
4.1 Topography, geology, hydrogeology and hydrology

The site lies between an elevation of about 65 and 78 m. There is a general slope downwards from west to east along the spine of the site, which forms a shallow valley feature (originally accommodating a railway siding for the chemical works).

The natural geology of the Cranleigh area is composed of zones of constructed sand bedrock deposit, with a high presence of Weald clay (a sequence of mudstones, clays and occasional sandstones which is some 150 m thick in this area (www.9)).

Leachable physical and chemical contaminants flow across/near the surface of the site arriving by gravity at the leachate lagoon, which has a capacity of 13,000 m³ – the rectangular lagoon (location A) in Figure 4-1 and Figure 4-2. Once the leachate arrives in the leachate lagoon it is stored until there is space in the middle lagoon (location B, with a capacity of 3,000 m³). The middle lagoon was constructed in 1970 to enable effluent treatment and is also fed by an overflow from the quarry lagoon (location C with a capacity of 100,000 m³).

![Figure 4-2 Cranleigh Site showing leachate lagoon (A)](image)

4.2 Sampling Methodology and Material Application

Samples were collected on 11th March 2014 from different locations of the site, including upstream of the industrial discharge (brick shed and wood drain), inflow to the leachate lagoon, middle lagoon and quarry lagoon. All water samples
(typically 1-5 litres) were then filtered (Whatman No 1) and stored at 4 °C. Aliquots of each untreated sample were analysed by inductively coupled plasma mass spectrometry (ICP-MS) to detect the initial level of trace elements at each location (refer to section 2.7).

Following this and with a view to remediate the chemical contamination on this site, a series of laboratory experiments were undertaken using Blueguard® 63, G1-3 and G1-3C materials on filtered water from the leachate lagoon (Figure 4-2). Considering the findings of the experiments in section 3.4.2, batch equilibrium trials were set at 15, 45 and 60 min contact times for a mass of 0.25 g for each Blueguard® material and using a 50 ml of the leachate water lagoon sample. The leachate lagoon water sample was investigated under both undiluted and diluted conditions (necessary to ensure that the initial elemental levels were within the linear dynamic range of the ICP-MS calibration curve). Furthermore, a series of field-based (batch equilibrium and column) experiments were undertaken in an area adjacent to the leachate lagoon. This was carried out to evaluate the potential of the material under field-based conditions to treat the water from this site.

4.3 Laboratory Batch Experiments for the Treatment of Trace Elements in Water Samples from the Cranleigh Industrial Site

In the first experiment the filtered water samples collected from the various sites at Cranleigh were diluted with distilled deionised water (DDW) prior to analysis by ICP-MS. This was carried out as the samples were expected to have a high level of trace elements that may be above the elemental calibration range for the ICP-MS instrument (0 to 750 µg l⁻¹). The samples were diluted as follows as shown in Table 4-1.

<table>
<thead>
<tr>
<th>Location</th>
<th>Dilution Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brick Shed</td>
<td>1000x</td>
</tr>
<tr>
<td>Wood Drain</td>
<td>1000x</td>
</tr>
<tr>
<td>In-flow to Leachate Lagoon</td>
<td>1000x</td>
</tr>
<tr>
<td>Leachate Lagoon</td>
<td>100x</td>
</tr>
<tr>
<td>Middle lagoon</td>
<td>100x</td>
</tr>
<tr>
<td>Quarry lagoon</td>
<td>100x</td>
</tr>
</tbody>
</table>
4.3.1 Results and discussion

The trace element levels determined in the various water samples from the Cranleigh site are shown in Table 4-2. The data shown is for zinc and manganese only as, all of the other elements (Al, As, Cd, Cr, Co, Cu, Fe, Pb, Ni, Se and V) were below the detection limit. The zinc levels range from 2.11 to 111.42 mg l\(^{-1}\) with the highest concentration being found in the brick shed water drain sample. Similarly, the manganese levels ranged from 0.58 to 26.71 mg l\(^{-1}\), with the highest value for the wood drain sample. The only other element to have elevated levels throughout this site is aluminium, in the range 0.59 to 2.72 mg l\(^{-1}\). These values are all high with respect to the acceptable levels based on the World Health Organisation (WHO) guidelines for drinking water, for zinc (5000 µg l\(^{-1}\) Zn) and manganese (50 µg l\(^{-1}\) Mn), respectively (refer to section 1.2). Therefore, remediation measures need to be undertaken to reduce the levels of these trace elements, especially Zn and Mn for the surface water samples collected at Cranleigh.

<table>
<thead>
<tr>
<th>Element</th>
<th>LOD (^{1})</th>
<th>Brick shed</th>
<th>Wood drain</th>
<th>In-flow to leachate lagoon</th>
<th>Leachate lagoon</th>
<th>Middle lagoon</th>
<th>Quarry lagoon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.02</td>
<td>13076.9</td>
<td>26707.8</td>
<td>9489.1</td>
<td>2843.4</td>
<td>2089.6</td>
<td>576.1</td>
</tr>
<tr>
<td>Zn</td>
<td>0.7</td>
<td>1111420.7</td>
<td>255563.7</td>
<td>101029.9</td>
<td>25946.8</td>
<td>19575.5</td>
<td>2111.9</td>
</tr>
</tbody>
</table>

\(^{1}\) limit of detection for each element measured using ICP-MS (µg l\(^{-1}\))

The next set of experiments focused on the potential treatment of water from the leachate lagoon as this site represented the highest levels for the three lagoons. Moreover, whilst the water from the brick shed and wood drains, and in-flow to the leachate lagoon had very high Zn and Mn levels, the volume of water from these sampling sites is minimal and subjected to seasonal variation. As in theory, the effect of the wet season and subsequent dilution of the lagoons can occur as a result of the rain.

As the original diluted leachate lagoon sample (100x dilution) was well within the calibrated range for the ICP-MS instrument, and in order to minimise the amount of dilution, the original leachate lagoon sample was diluted 15x to be used as a control sample for comparison. However, with the samples contacted with the
Blueguard® materials, only 4x dilution was required. This was done to bring the range with calibration of the instrument.

**pH study on zinc and manganese removal**

As discussed in section 1.3.5 and experimentally in section 3.2.1, the pH of the solution may affect the solubility of trace elements and their bioavailability in biological systems. The pH of the leachate lagoon solution (pre-treatment) was measured and recorded (7.2). The pH was then changed to 2, 9 and 10 using 1% HNO₃ (Trace analysis grade, Fisher Scientific UK) and NaOH(aq) (0.1 mol dm⁻³, trace element grade, Fisher scientific, UK). An aliquot of each solution was then analysed by ICP-MS. This experiment was carried out to study and compare the removal of trace elements in the water from the leachate lagoon as a result of possible precipitation by pH adjustment. This is important so as to assess the findings of the subsequent experiments to treat the contaminated water with the Blueguard® materials.

The filtered leachate lagoon water samples were re-analysed and values were determined for zinc (26.6 mg l⁻¹ Zn) and manganese (1.768 mg l⁻¹ Mn). Figure 4-3 shows the effect of changing the pH level of the leachate lagoon water. Initially, changing the pH to 2 resulted in no significant change in the levels of Zn or Mn in the leachate lagoon water. At pH 9 there is some evidence of a slight reduction, with measureable levels of elemental precipitation. However, at pH 10 a significant reduction occurred, shown as the % level of elemental precipitation in Figure 4-3. This finding is supported by Shim et al., (2014) and Orlov et al., (2013), who state that increasing the levels of hydroxide ions in solution (to pH levels of 9 -10) may result in the precipitation of metal hydroxide. Moreover, it demonstrates that increasing the pH of the solution with OH⁻ ions has an effect on these two elements. It should also be stated that these pH levels are not normally associated with ‘natural’ water sources (ground, surface or artesian).
Removal of manganese and zinc from leachate lagoon using Blueguard®

Applying Blueguard® materials to the leachate lagoon samples resulted in the removal of only 33% of manganese from the solution. However, these materials reduce the level of zinc by ca. 7-fold (~85% removal) within 15 min contact time (see Figure 4-4). This finding is of particular importance as the World Health Organization (WHO) states a legal limit of zinc in drinking water of 5 mg l⁻¹ and these materials could very well reduce the level of zinc below this amount (to 3.5 mg l⁻¹) (Shobana et al., 2015).

This experiment followed the same trend for both elements in terms of the effect of contact time, with longer times than 15 min not improving removal efficiency, and showing that all types of Blueguard® materials have similar removal efficiency for each trace element.
4.4 Laboratory Batch Experiments for the Treatment of Trace Elements in Undiluted Solution

Based on the results in the previous experiment it was clear that the initial level of zinc is very high and above the ICP-MS calibration range. However, in order to study the effect of Blueguard® materials on the other trace elements in the samples taken from the lagoons, analysis on an undiluted Cranleigh solution was undertaken. In this set of experiments, the detection of zinc was removed from the ICP-MS run procedure so as to protect the detector.

4.4.1 Results and discussion

Diluting the samples taken from different locations at the Cranleigh site resulted in an undetectable level of aluminium, cadmium, chromium, copper, iron, lead and nickel (refer to Table 4-2). However, running the samples without dilution clearly showed the presence of these elements in water samples from the different locations (Table 4-3). Apart from one location (Wood drain), the levels of aluminium and iron in different locations was below the level allowed by the WHO (200 µg l⁻¹ Al and 300 µg l⁻¹ Fe). On the other hand, the levels of cadmium and manganese were above the guideline limits of the WHO, namely, with 5 µg l⁻¹ Cd and 400 Mn µg l⁻¹, except for the quarry lagoon site.

The levels of chromium, copper, and lead were below the WHO limits for drinking water (50 µg l⁻¹ Cr, 2000 µg l⁻¹ Cu and 10 Pb µg l⁻¹) at all locations.

Table 4-3 Levels (average of 6 replicates) of water samples (µg l⁻¹) from the Cranleigh Leachate and Brickworks (collected 11th March, 2014) analysed (without dilution) by ICP-MS, University of Surrey

<table>
<thead>
<tr>
<th>Element</th>
<th>LOD¹</th>
<th>Brick shed</th>
<th>Wood drain</th>
<th>Inflow to leachate lagoon</th>
<th>Leachate lagoon</th>
<th>Middle lagoon</th>
<th>Quarry lagoon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.0</td>
<td>102</td>
<td>300</td>
<td>4.60</td>
<td>126</td>
<td>8.24</td>
<td>15.5</td>
</tr>
<tr>
<td>Cd</td>
<td>0.03</td>
<td>118.66</td>
<td>157</td>
<td>87.7</td>
<td>22.5</td>
<td>14.2</td>
<td>0.03</td>
</tr>
<tr>
<td>Cr</td>
<td>0.03</td>
<td>0.49</td>
<td>0.03</td>
<td>0.15</td>
<td>0.76</td>
<td>0.13</td>
<td>0.08</td>
</tr>
<tr>
<td>Cu</td>
<td>0.03</td>
<td>1.38</td>
<td>3.83</td>
<td>2.80</td>
<td>43.96</td>
<td>2.52</td>
<td>1022.05</td>
</tr>
<tr>
<td>Fe</td>
<td>0.06</td>
<td>18.11</td>
<td>648.49</td>
<td>48.36</td>
<td>211.84</td>
<td>14.65</td>
<td>46.81</td>
</tr>
<tr>
<td>Pb</td>
<td>0.02</td>
<td>9.01</td>
<td>2.50</td>
<td>1.14</td>
<td>3.74</td>
<td>0.31</td>
<td>57.5</td>
</tr>
<tr>
<td>Mn</td>
<td>0.02</td>
<td>6240.95</td>
<td>10676.16</td>
<td>4915.64</td>
<td>1969.39</td>
<td>1368.27</td>
<td>248.36</td>
</tr>
<tr>
<td>Ni</td>
<td>0.02</td>
<td>2408.32</td>
<td>369.4</td>
<td>179.3</td>
<td>40</td>
<td>39.31</td>
<td>6518</td>
</tr>
</tbody>
</table>

¹ limits of detection for each element measured using ICP-MS (µg l⁻¹)
Trace element removal (excluding zinc) from the leachate lagoon

It was clear from the results in section 4.3 that increasing the contact time beyond 15 min did not have any additional remedial benefit. Therefore, this experiment was modified by using 0.25 g of Blueguard® 63, G1-3 and G1-3C for only 15 min contact time and applied to the undiluted leachate lagoon samples (Table 4-4).

<table>
<thead>
<tr>
<th>Trace Element</th>
<th>Blueguard® 63</th>
<th></th>
<th></th>
<th></th>
<th>Blueguard® G1-3</th>
<th></th>
<th></th>
<th></th>
<th>Blueguard® G1-3C</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Removal (%)</td>
<td>DM¹</td>
<td></td>
<td></td>
<td>Removal (%)</td>
<td>DM¹</td>
<td></td>
<td></td>
<td>Removal (%)</td>
<td>DM¹</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>97.9</td>
<td>0.2</td>
<td></td>
<td></td>
<td>94.5</td>
<td>0.3</td>
<td></td>
<td></td>
<td>94.7</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>13.5</td>
<td>1.2</td>
<td></td>
<td></td>
<td>11.1</td>
<td>3.7</td>
<td></td>
<td></td>
<td>11.0</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>89.2</td>
<td>1.2</td>
<td></td>
<td></td>
<td>90.3</td>
<td>0.1</td>
<td></td>
<td></td>
<td>91.0</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>41.4</td>
<td>0</td>
<td></td>
<td></td>
<td>40.8</td>
<td>1.3</td>
<td></td>
<td></td>
<td>42.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>30</td>
<td>1.3</td>
<td></td>
<td></td>
<td>28.3</td>
<td>8.3</td>
<td></td>
<td></td>
<td>33.1</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

¹Deviation from mean

As well as removing a high level of zinc from the leachate lagoon sample (Figure 4-4), Blueguard® materials could remove more than 90% of aluminium and iron in the solution. Around 40% of manganese was removed using these materials; the manganese concentrations are close to the values obtained when the solution was diluted (Table 4-2 and Figure 4-4). Blueguard® materials were not, however, capable of removing significant levels of the cadmium in the solution (only around 10% removal), nor any of nickel and chromium. This may be due to the high level of zinc in the solution and therefore the higher tendency of free zinc ions in the solution to bond with released hydroxide ions from the Blueguard® materials (selective precipitation of zinc hydroxide). Despite a very low level of lead, removal of this element using Blueguard® materials took place. All three types of materials had similar removal efficiency in this experiment.

4.5 Investigation on the exhaustion point of Blueguard® G1-3

A better understanding of the exhaustion point or reduction in removal efficiency of Blueguard® G1-3 was sought. In this section, samples from the leachate
lagoon were collected (May-2016) and trace element analysis were carried out prior to contact with the Blueguard®. Matching the design of the previous experiment in section 4.4 (mass / volume), 1 g of Blueguard® G1-3 was mixed with 200 ml solution from the Cranleigh lagoon using the mechanical shaker for 15 min. Next, the Blueguard® G1-3C used in the previous step was separated from the mixed solution. The used Blueguard® G1-3C was then reused and contacted with another 200 ml of new leachate lagoon solution for 15 min. This process was repeated up to 25 times, resulting in 1 g of the same material being reused to treat, a cumulative, 5 litre of sample solution taken from the leachate lagoon.

4.5.1 Results and Discussion

The filtered leachate lagoon water samples were analysed and values were determined for manganese (3.05 mg l⁻¹ Mn) and zinc (34.30 mg l⁻¹ Zn). These values are higher compared to the previous sampling in March 2014, which had occurred on a heavily rainy day with calculated levels of 2.59 and 25.94 mg l⁻¹ for manganese and zinc, respectively; this can be related to the effect of rain and subsequently the dilution in the level of these trace elements in the leachate lagoon.

As Figure 4-5 shows, Blueguard® G1-3 could remove 22% of manganese and 71% of zinc from the solution under the first application of this mass (1 g) of the material. The better removal efficiency for zinc compared to manganese can be related to higher pK values for product of zinc (16.2) compared to that of manganese (12.7); thus more zinc was removed from the solution compared to manganese (Orlov et al., 2013). After the second use of the material 17% and 42% of manganese and zinc were removed from the solution, respectively. The efficiency of Blueguard® G1-3 dropped below 10% and 20% for manganese and zinc, respectively after the 10th use of Blueguard® G1-3. It took 16 contact periods (and a total volume of 32 l) for manganese to be completely removed from the solution and 24 periods (total volume of 4.8 l) for the removal efficiency for zinc to reach ~2.8%.
In order to design a full scale plant for the remediation of this site and to test the applicability of this project to a real world scenario, two on-site (field) experiments were carried out.

### 4.6 Field Studies (Dynamic and Static) for Treatment of Trace Elements

Experiments carried out in the laboratory confirmed that Blueguard® materials could be applicable for the remediation of high levels of trace elements at the site before the contaminated water from this site flows into a local stream with subsequent discharge into a major Surrey river-water body. However, results

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Figure 4-5 Exhaustion point of 1g of Blueguard® G1-3 for Mn and Zn after 15 min contact in 200 ml leachate lagoon solution, repeated 25 times (total 5 litres)
obtained under laboratory conditions might not reflect real world applicability of these materials for the large scale purposes, such as the remediation of a contaminated site as large as the Cranleigh Brickworks. For this reason, another set of experiments were designed specifically for on-site field exploitation in order to test the efficiency of the materials under different conditions (column and scaled-up batch equilibrium).

4.6.1 Dynamic systems - Column

Traditionally the testing of a solid phase material is undertaken using batch equilibrium conditions. However, in nature a contaminated water sample may pass through a solid phase (such as soil or sediment). As such, there may be a different ‘rate of interaction or mixing’ of the chemical components in the wastewater with the particle sizes of the solid as the liquid passes down through the material. In order to evaluate this, a column separation experiment was design for application on-site at Cranleigh. Hence, the following was chosen as a dynamic system study method using a column of the material contained in a glass tube.

For this type of experiment, Blueguard® G1-3 was packed into a column and washed with deionized water using a continuous flow in order to settle the bed of the solid phase in the column (to eliminate air pockets). The solution from the leachate lagoon was then fed through the column providing a fixed head of solution on top of the packed Blueguard® G1-3 (150 g) material. A constant flow rate (3.34 ml / min) of the lagoon water was applied at the top of the column using a separating funnel and the stopcock before discharge into the reception vessel (Figure 4-6). Sixteen fractions (each of 50 ml that had passed through the column) were collected, and transferred to the laboratory, each then diluted 20 times with DDW and analysed by ICP-MS.
4.6.2 Static systems

In order to evaluate a scaled-up version of the laboratory batch equilibrium experiments, 150 g Blueguard G1-3 was added to a bucket containing 4 litres of wastewater from the leachate lagoon. A rotary hammer drill with drill bit attached to the end was applied to the mixture to agitate the solution and material for 15 min. After every 15 min of agitation by the drill, a 250 ml aliquot of treated water was removed from the bucket, filtered, diluted 20 times and stored for analysis. A further 250 ml solution from the leachate lagoon was added to the bucket to simulate a constant input of solution, as would happen in the field with a large scaled-up system. This procedure was carried out eight times to understand the potential exhaustion limit of the material.
4.6.3 Results and discussion

**Dynamic system**

Analyses were carried out on the filtered solution (fraction) collected from the column shown in Figure 4-6, using the procedure in section 4.6.1. The results showed that more than 95% of zinc and 65% of manganese were removed from the leachate lagoon (Figure 4-8).

![Mn column](image)

![Zn column](image)

*Figure 4-8 Removal (%) of manganese (a) and zinc (b) using dynamic system containing 150 g Blueguard® G1-3 in the field, Cranleigh site*

Using this column separation methodology, the first fraction had the lowest detectable level of zinc (99% removal of Zn) for the wastewater from the leachate lagoon. This suggests a higher level of hydroxide ions released to the sample, forming zinc hydroxide compounds (Figure 4-8). Better removal efficiency was obtained using this dynamic system design compared with batch experiment as
outlined in sections 4.3 and 4.4. Application of the Blueguard® materials under batch experiment conditions in the laboratory resulted in around only 80% and 30% removal of zinc and manganese present in the leachate lagoon, respectively. This may be due to the flow of the contaminated water through a column containing 150 g Blueguard® G1-3 having a better retention time enabling a higher separation efficiency. As such there may be more equilibrium exchanges of the zinc and manganese with the material, enabling a release of hydroxide ions, thereby the formation of zinc or manganese hydroxide. Another substantial outcome of this experiment was the re-applicability of Blueguard® G1-3 as different fractions of leachate lagoon were passed through the column containing the exact same Blueguard® material for each fraction.

**Static system**

Using a field based scaled-up batch equilibrium procedure (as outlined in section 4.6.2 and Figure 4-9) it was possible to remove 95% of zinc from the leachate lagoon wastewater. From an initial leachate lagoon level of 26,864.7 µg l⁻¹ Zn mixing with the material in the bucket resulted in a level of 723.5 µg l⁻¹ Zn. As shown in Figure 4-9 (b), the different batch solutions (of 250 ml) after mixing with the 150 g of material indicate a constant removal of zinc from the wastewater. Similarly, the field-based system was more efficient at removing manganese (97%) than the laboratory experiment (33%). Furthermore, Figure 4-9 (a) clearly shows the impact of this procedure in removing manganese. Two possible explanations for the higher removal efficiency in the field-based experiment are (1) the higher dose of Blueguard® G1-3 material used in the bucket and (2) the method of mixing (using a high speed drill). Clearly, this experiment has produced encouraging results about the potential use of Blueguard® G1-3 for a full scale on-site facility using the batch equilibrium. Moreover, after the removal of 1 l of treated wastewater from the bucket, the 150 g of Blueguard® G1-3 was still effectively removing these trace elements.
Figure 4-9 Removal (%) of manganese (a) and zinc (b) using static system containing 150 g Blueguard® G1-3 in the field, Cranleigh site

4.7 Mechanism

Blueguard® materials were characterised after contact with leachate lagoon water using X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques (as described in sections 2.3, 0 and 2.6 respectively). These experiments were carried out in order to understand and clarify the possible mechanism by which these materials contribute to reducing the level of trace elements in the solution.
4.7.1 Results and discussion

X-ray fluorescence spectrometry (XRF) analyses were carried out after Blueguard® materials were applied to leachate lagoon water. Table 4-5 compares the percentage elemental composition present in Blueguard® materials before and after contact with leachate lagoon water (laboratory and field-based experiments). As these results show, a negligible change was observed in the Blueguard® materials after contact with the contaminated solution suggesting that the ions which have been removed from the solution did not enter into nor attached to the surface of the materials. In another words the Blueguard® materials do not remediate contaminants using any forms of sorption as a removal mechanism.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Blueguard® 63</th>
<th>Blueguard® G1-3C</th>
<th>Blueguard® G1-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>41.72</td>
<td>39.78</td>
<td>39.36</td>
</tr>
<tr>
<td></td>
<td>After contact with leachate lagoon + (%)</td>
<td>After contact with leachate lagoon + (%)</td>
<td>After contact with leachate lagoon + (%)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.88</td>
<td>0.53</td>
<td>0.49</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.62</td>
<td>6.43</td>
<td>6.47</td>
</tr>
<tr>
<td>Mn₃O₄</td>
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<tr>
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<td>44.47</td>
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<tr>
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<tr>
<td>Cr₂O₃</td>
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<td>0.33</td>
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<tr>
<td>ZnO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

*Laboratory based experiments

X-ray diffraction (XRD)

Figure 4-10 to Figure 4-12 compare the different materials, namely, Blueguard® 63, G1-3 and G1-3C (respectively) before and after contact with leachate lagoon water. The results show that although the application of Blueguard® materials can remediate the level of trace elements in the contaminated water sample, the mineral structure of these materials remain unchanged. These results suggest that the Blueguard® materials do not remove any trace elements from leachate lagoon water via an ion exchange mechanism. This hypothesis is based on the
fact that the mineral composition and compounds present in these materials are identical before and after contact with this type of contaminated water sample.

**Figure 4-10** XRD Diffraction results for Blueguard® 63 before and after contact with leachate lagoon wastewater

**Figure 4-11** XRD Diffraction results for Blueguard® G1-3 before and after contact with leachate lagoon wastewater
Brunauer-Emmett-Teller (BET) studies

A series of Brunauer-Emmett-Teller (BET) experiments were carried out (refer to section 2.5) in order to understand the porosity of Blueguard® materials. Further investigations were also undertaken using this technique to study the adsorption behaviour on the surface of these materials. This was done by comparing the pore width of each Blueguard® material against the surface area before (blue line) and after contact (red line) with leachate lagoon wastewater. The plotted curve represents the pore distribution of the materials.

Figure 4-13, shows the results for Blueguard® 63 and it can clearly be seen that the curves overlap, which suggests that there is very little loss of material as a result of contact with the wastewater. The specific surface area for this material before and after contact with leachate lagoon wastewater were given by the output of the software as 4.0235 and 4.6339 m² g⁻¹ respectively, with typically ±10% uncertainty for each experiment. Considering the difference between these two values (15 %) it is within an acceptable error range (< 2x10 %). Furthermore,
it can be concluded, based on these findings, that adsorption was not the mechanism by which this material removed contaminants from polluted samples.

![Pore size distribution comparison of Blueguard® 63 before and after contact with leachate lagoon wastewater](image)

Figure 4-13 Pore size distribution comparison of Blueguard® 63 before and after contact with leachate lagoon wastewater

The pore size distribution of Blueguard® G1-3 (Figure 4-14) before and after contact with the leachate lagoon wastewater were similar. However, the total pore volume (integrals under the curves) for Blueguard® G1-3 decreases after contact. This may be a result of the loss of “fines” due to contact with the water, meaning after contact the particles are on average larger and the specific surface area therefore decreases. The specific surface area for this material before and after contact with the wastewater was 4.99 and 3.90 m² g⁻¹, respectively. The difference between these values (21 %) is not far from the acceptable error range (2x10 %), thus it can be assumed that the surface area remained unchanged and the adsorption of contaminants onto the surface of the material did not take place.
Figure 4-14 Pore size distribution comparison of Blueguard® G1-3 before and after contact with leachate lagoon wastewater

Figure 4-15 Pore size distribution comparison of Blueguard® G1-3C before and after contact with leachate lagoon wastewater

After mixing the Blueguard® G1-3C materials with the leachate lagoon wastewater, a substantial loss of pore volume of less than 75 angstroms pore
diameter occurred (see Figure 4-15). The specific surface area of this material before contact with the water was 12.51 m$^2$ g$^{-1}$. This value is substantially higher than that for the Blueguard® 63 and Blueguard® G1-3. This is not surprising since the Blueguard® G1-3C contains activated carbon and thus a higher specific surface area. This value, however, decreased to 5.77 after contact with the leachate lagoon wastewater. These findings suggest that the carbon content has decreased after contact with the water, with the carbon floating to the top of the solution and staying in suspension. This was noted during the removal of the liquid at the end of the experiment. Therefore, it is believed that loss of pore volume and a decrease in specific surface area is not due to the adsorption of trace element contaminants but through loss of carbon into the treated solution.

### 4.8 Summary

The purpose of this chapter was to analyse and remediate the wastewater from a contaminated site located in Cranleigh, Surrey. This site was of particular interest as it is designated as a “Special Site” under the Environmental Protection Act 1990 by the local authority. Sampling activities were undertaken at different locations of the former brickworks, starting at surface water locations near the Brickwork factory (dating back to 200 years ago) and then at three lagoons designed to store and dilute the chemically contaminated surface water (evident at some sites by the ‘blue’ coloration of the lagoon water). Results showed elevated levels of cadmium, manganese and zinc at most sampling locations. It was therefore decided to evaluate the use of the Blueguard® materials as a remediation option utilising field-based separation procedures (refer to section Figure 4-6). Samples from the leachate lagoon (Figure 4-2) were chosen as this site was the storage pond with the highest level of trace elements. Laboratory-based and field-based experiments were carried out. Laboratory-based batch equilibrium results revealed that the Blueguard® materials could remove around 95, 90, 40, 30 and 85% of the aluminium, iron, manganese, lead and zinc levels from the leachate lagoon wastewater (refer to sections 4.3.1 and 4.4.1).

A set of experiments was carried out to understand the extent at which the materials stop being efficient at removing the high level of manganese and zinc. While Blueguard® G1-3 could remove 22% of manganese and 71% of zinc from
the solution under the first application; the efficiency of the material dropped below 10% and 20% for manganese and zinc, respectively following the 10th contact period or use of Blueguard® G1-3 (section 4.5.1).

In the field, two different types of experiments (dynamic and static) were designed and carried out using the Blueguard® G1-3. As the level of zinc and manganese were very high in the leachate lagoon wastewater, focus was set on remediating the level of these two elements. The results indicate that the application of Blueguard® materials, using these methods, on the leachate lagoon wastewater can successfully remediate the levels of zinc and manganese. As such, 99% of zinc and 65% manganese were removed from the leachate lagoon water using the dynamic system (column experiment) and 95% zinc and 97% manganese were removed using the static system (a scaled-up batch equilibrium experiment).

The experiments carried out in this chapter demonstrate the applicability of the Blueguard® materials in remediating contaminated water.

Attention was paid specifically to the mechanism by which these materials remove trace elements from contaminated water. A set of experiments including XRF, XRD and BET were carried out on the Blueguard® materials (laboratory and field-based experiments) before and after contact with the leachate lagoon wastewater. The aim of this was to evaluate whether any possible changes to the composition or surface of the Blueguard® materials occurred after contact with the Cranleigh Brickworks surface water. The results suggest that the mineral structure, composition and specific surface area of these materials do not change as a result of contact with contaminated water. Therefore, the reduction of trace elements in the contaminated water on applying these materials was not the result of mechanisms such as ion exchange, adsorption or absorption (refer to 4.7.1). The increase in the pH level of DDW after addition of these materials suggests the release of hydroxide ions, resulting in the formation and precipitation of insoluble hydroxide compounds. The addition of the Blueguard® materials to the contaminated water did not increase the pH. This finding reinforces the assumption that possible precipitation of specific trace elements in the water as a result of contact with the Blueguard® materials occurs by forming
insoluble hydroxide compounds. This results in non-available hydroxide ions (as in the case of DDW) which will then not result in an increase in solution pH. The ability of the different types of the Blueguard® materials to remove specific trace elements, especially zinc and manganese (as shown in this chapter), does not appear to be influenced significantly by particle size (Blueguard® 63 and Blueguard®G1-3) or the presence of carbon (Blueguard®G1-3C).
Chapter 5  Conclusion and Further Investigation

Water is vital to life. It is required by humans, plants and animals for drinking and hygiene. Aquatic lifeforms require it for their habitat, industries use it for a range of processes (such as reactant / product in reactors, a mass-separating agent in separation processes in the utility system, in boilers and cooling towers) (Huang et al., 1999). Further, it is also used for equipment cleaning, firefighting, and various miscellaneous consumptions, and there are many further uses.

Contaminated water can be toxic and imposes a threat to all life. Therefore, it is highly important to address the factors that degrade the quality of water and to take measures to control and remediate contaminated water. Domestic and industrial applications of water along with the contamination of rainwater as a result of road or farmland pollution are some of the main factors contributing to the deterioration of water quality (Tebbutt, 1998). The most complex form of pollution is from industrial wastewaters, which include many chemical contaminants and heavy metals (Fergusson, 1982). Heavy metals (and trace elements) contamination is mainly of importance as these metals following anthropogenic input into water are potentially toxic to animals and humans.

Diversity in the sources and types of physical, chemical and biological contaminants has resulted in the development and application of a range of treatment methods and techniques. In recent years there has been an increasing interest in the application of different types of solid phase materials for water treatment. The types of solid phase materials that have been studied include zeolites, activated carbon, and lignite (refer to 1.4.1). These materials can be used to remove contaminants namely trace elements with the related disadvantages of not being available for all heavy metals and the high operational cost (Kurniawan et al., 2006). The aim of this study was to investigate a novel alternative type of material, namely Blueguard® materials (refer to 2.2), for water treatment purposes and which have the potential of being both effective and fast for treating complex chemically-contaminated waters (including the presence of trace elements, organics, ions, etc.).
5.1 Thesis Summary

In this research contaminated waters from two different sources have been analysed and the evaluated through contact (batch equilibrium and column separation) with Blueguard® materials so as to remediate the levels of chemical contamination of wastewaters. The following have been investigated:

(1) candidate materials (Blueguard® materials) were provided and characterised using a set of different techniques (refer to Chapter 2). This was carried out to understand the mineralogy, structure, porosity and composition of these materials (refer to sections 2.3, 2.4, 2.5). Furthermore, it was necessary to evaluate whether these materials are safe options to use in the environment and do not release harmful elements to water (refer to 2.7.3);

(2) the efficiency of the Blueguard® materials in reducing the levels of trace elements from laboratory prepared contaminated solutions was studied: a) using stock solution (section 3.2) and b) using rainwater with added digested motorway dust (section 3.4).

(3) the applicability of the Blueguard® materials for the treatment of an industrial discharge, from a contaminated site in Cranleigh, Surrey, was investigated under laboratory condition (sections 4.3 and 4.4), the exhaustion point of the materials was also examined (section 4.5) to understand the point at which the materials are no longer capable of removing contaminants from the solution as well as using both a scaled-up field-based batch equilibrium and a column separation procedure (section 4.6)

(4) the possible removal mechanism for trace elements using three types of Blueguard® materials was evaluated using samples pre- and post-treatment of a Cranleigh leachate lagoon wastewater containing high levels of zinc and manganese (section 4.6).

5.1.1 Blueguard® exploration and characterisation

The Blueguard® materials are olivine-rich materials sourced from rock and were provided by Sibelco Nordic Deposits of Åheim, Norway. X-ray fluorescence spectrometry (XRF) was used for the determination of the chemical composition of three different types of Blueguard® materials (refer to section 2.3). Based on this technique SiO₂, MgO, Al₂O₃ and CaO were found to be the major
components in these materials. Brunauer–Emmett–Teller (BET) analyses were carried out to study the surface area and porosity of these materials (refer to section 2.5). The relevant results showed that the Blueguard® materials are non-porous with weak adsorbent-adsorbate interactions. X-ray Diffraction (XRD) was employed to characterise and confirm the main compounds present in the Blueguard® materials (refer to section 2.4). The data showed that the main compounds are alteration products of Mg-rich silicates, namely olivine, talc, clinochlore, antigorite, biotite and ferroactinolite. Blueguard® materials are labelled as Blueguard® 63, Blueguard® G1-3 and Blueguard® G1-3C. Blueguard® 63 is a fine grained mineral (flour texture), whereas Blueguard® G1-3 and Blueguard® G1-3C are granulated forms of Blueguard® 63. Blueguard® G1-3C is the same as Blueguard® G1-3, except that it has the addition of some activated carbon.

Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the level of major and trace elements in the water samples, pre- and post-contact with the Blueguard® materials (refer to section 2.7). The results confirmed that all three Blueguard® materials are not a threat to the environment as they do not release any harmful compounds or elements (i.e. nickel, manganese) when in contact with water. These data provided important insights into the Blueguard® materials in terms of being a suitable and safe option for wastewater treatment.

5.1.2 Preliminary test and application of Blueguard® materials on polluted rainwater (non-point source pollution)

As the first step, and to ensure that Blueguard® materials are capable of removing trace elements from water, a multi-element (Cd, Cr, Cu, Fe, Pb, Mn, Ni and Zn) was prepared from commercial trace element stock solutions. The Blueguard® materials were then applied to this solution and the removal efficiency was evaluated under different pH (from 2 to 9) conditions. These studies were carried out under batch equilibrium conditions (shaking a known mass of solid with a volume of solution for a specific contact time) as outlined in sections 3.1 and 3.2.

The results showed that these materials are not efficient under acidic conditions (pH <3), however, by adjusting the pH value of the multi-element solution to 7 or
above different degrees of trace element removal were observed. The best elemental removals for this solution, at or above a pH value of 7, occurred for lead, zinc, copper and chromium over a range of 80% to 99%. Further studies confirmed that these materials were efficient under alkaline conditions (pH > 7 to 9), with the highest removal for lead (~ 90%) and the lowest removal efficiency being for manganese (~ 30%).

As mentioned in section 1.2, contaminants released to the environment come under two main categories point source pollution and non-point source pollution (EPA, 2012). In this research two types of samples were prepared as representatives of each category so as to test the efficiency of Blueguard® materials. One option was as an example of non-point pollution source, preparation and testing of a contaminated motorway stormwater using the batch equilibrium procedure. Contaminated water for this purpose was prepared by mixing a digested motorway dust sample with car park rain water and adjusting the pH to 7. A set of optimisation experiments, under batch equilibrium conditions (mass of solid, solution volume and contact time), was performed so as to obtain the best removal efficiency levels for the solution (refer to section 3.4.1).

Inductively coupled plasma mass spectrometry (ICP-MS) analysis confirmed that different levels of trace elements, including cadmium, chromium, copper, iron, manganese, nickel, lead and zinc were present in the simulated motorway stormwater sample. The results showed that a short contact time (less than 15 min) and only 0.25 g of the Blueguard® materials was required for reducing the levels of trace elements in the water. A negligible difference in efficiency was observed between the different types of Blueguard® materials. From around 80% (for manganese) up to 100% (for lead) removal of trace elements took place for different trace elements present in this water.

It is worth mentioning that, in contrast to adding Blueguard® materials to deionised distilled water (DDW) which resulting in a sizeable increase in pH (from 6 to 9.9), the pH value of contaminated water (modif-UoS CPW) remained around 7 after the application of these materials. This outcome suggests that the remediation of the contaminated rain water using Blueguard® materials was due to the precipitation of trace elements as result of the formation of insoluble metal
hydroxides. The fact that Blueguard® materials did not result in an increase in pH of previously contaminated water, despite the high removal efficiency, is of a great advantage.

5.1.3 Case study - Cranleigh Brickwork remediation (point source pollution)

The Cranleigh Brickworks is located in Surrey (UK) and has a long and chequered history of industrial activities (chemicals manufacturing operation and brick work activities) with significantly poor management. A detailed description of the site is mentioned in section 4.1. Industrial waste on this site has often been disposed of with little attention to the consequence of introduced contaminants and thus the site has been abandoned whilst being heavily contaminated. The site is listed as a Special Site No1 by the Environmental Protection Act 1990 by Waverley Borough Council (local authority).

This site was considered as a point-source water pollution for this study. Sampling, analyses and subsequently, the application of Blueguard® materials upstream of the industrial discharge of this site was carried out. Samples were taken from different locations and analysed by ICP-MS (Table 4-3). The results revealed that the levels of manganese and zinc present in the water are far beyond the limit (0.4 and 5 mg l\(^{-1}\) for Mn and Zn, respectively) set by the World Health Organization (WHO) guideline for drinking water. Among several lagoons on the site, the most contaminated one (leachate lagoon) was chosen and the removal efficiency of Blueguard® materials, under batch and column experiments were undertaken in the laboratory and at the field.

The results showed that by applying 0.25 g of Blueguard® materials to 50 ml of leachate lagoon water it was possible to remove up to 33% and 85% of manganese and zinc, respectively (within 15 min). This finding is of particular importance, since the WHO states a legal limit of zinc in drinking water of 5 mg l\(^{-1}\) and these materials could very well reduce the level of zinc below this amount (to ca. 3.5 mg l\(^{-1}\)).

Further investigation to evaluate whether it would be possible to use these materials on a large scale at the Cranleigh location was undertaken by setting up two types of experiment on the site, one a dynamic system and the other a static
system. Blueguard® G1-3 was packed in a column and the solution taken straight from the leachate lagoon was then continually fed into the column so as to maintain a fixed head of solution on top of the material. Blueguard® G1-3, as a filter, under this dynamic system could remove more than 95% of zinc and 65% of manganese.

A static system was designed using a bucket containing a mixture of contaminated discharge from the leachate lagoon and Blueguard® G1-3. A rotary hammer drill was used to agitate the mixture. More than 95% of zinc and up to 97% of manganese was removed from this industrial solution under this system. It was observed that Blueguard® materials not only performed well under laboratory conditions, but also showed good potential in removing contaminants from the polluted water in the field. Also, the application of Blueguard® materials under a static system in the field resulted in the best removal efficiency in comparisons with laboratory conditions and the dynamic system in the field.

5.1.4 Removal mechanism

Understanding the mechanism by which Blueguard® materials remove the contaminants from the solution was another area which needed to be explored. Therefore, the same series of techniques which were carried out to characterise the materials (XRF, BET and XRD) were repeated for all three types of Blueguard® materials after these materials had been applied to the leachate lagoon water. The results were then compared to the equivalent data before contact with water samples containing trace elements (refer to sections 2.3.2, 2.4.2 and 2.5.2). These comparisons showed that the mineral analysis of these materials does not change after contact with trace elements in solution. This is interpreted to be that the Blueguard® solids are not ion exchange materials and do not remove trace elements via chemisorption (refer to Chapter 1 sections 1.3.6 and 1.3.7). It was found that the specific surface area of these materials did not change, indicating that that the adsorption of trace elements did not take place using Blueguard® materials. In general, the chemical composition of the Blueguard® materials remained unchanged and thus no change in mineralogy of the materials was observed. On the other hand, as previously explained, the addition of Blueguard® materials to DDW resulted in an increase in the value of
pH (Table 3-2). It was postulated that this was due to the release of hydroxide ions from the surface of the material to the solution. Therefore, it appears that the treatment of contaminated water takes place due to the release of hydroxide ions from Blueguard® materials and thus precipitation of the trace elements from the solution. However, there is a chance that characterisation techniques might not have been sensitive enough to detect elements that contaminate the surface of the materials. Further investigations with regards to additional characterisation techniques will be discussed in the future work section.

5.1.5 The application and advantages of Blueguard® materials in wastewater treatment technology

The results showed that these materials can remediate contamination from both sources of polluted water by causing the dissolved trace elements to precipitate from solution. Therefore, based on the proposed mechanism by which Blueguard® materials perform (as discussed in 1.3.4), these materials can be considered as one the solid phase materials used for chemical wastewater treatment (refer to 1.4) and can be good fit in chemical unit process. Chemical precipitation can be unsuccessful when the levels of metal ions in solution are below 100 mg l⁻¹ (Cechinel, et al., 2016; Kumar et al., 2015; Nourbakhsh et al., 1994). Moreover, the Blueguard® materials were efficient in removing trace elements from the solution within the levels ranging from 1.7 µg l⁻¹ Pb (refer to 3.3) to 26 mg l⁻¹ Zn (refer to 4.3). Therefore, the application of Blueguard® materials may be an effective technique for the removal of metal ions present at low levels. On the other hand, technologies such as ion exchange, membrane separation and adsorption processes using activated carbon can be extremely expensive and thus unfeasible for the treatment wastewater in large scale (high volumes) with low levels of ions (Wang & Chen, 2009). The materials in this study are by-product materials and can be considered to be relatively low cost. This means that Blueguard® materials may be fit-for-purpose in developing countries, where local cost, effective water treatment is very important.

5.2 Recommendations for Future work

The results presented here have demonstrated the effectiveness of Blueguard® materials in removing trace elements from wastewater. However, these materials
could be further studied and their application in wastewater treatment could be further developed in a number of ways as described in the next subsections.

5.2.1 Extending characterisation investigations

The results obtained in section 4.5 suggested that the reapplication of Blueguard® G1-3 with contaminated solution resulted in exhausting the material, reaching its limit for removal of the trace elements manganese and zinc. In order to have additional data to support the views proposed on the mechanism by which these materials remove trace elements from the solution, it would be required to follow the same characterisation techniques that were used in section 4.7 (on non-exhausted materials).

So far, based on the effect of the Blueguard® materials on the pH value of distilled water, it was concluded that these materials release hydroxide ions into the solution resulting in specific trace element precipitation. X-ray photoelectron spectroscopy (XPS) technique can be used to further investigate this hypothesis (Bluhm, 2011). This technique, by providing information on binding energy (BE) related to oxygen and of hydroxide, would make it possible to compare any changes in the level of oxygen and hydroxide present in the surface of Blueguard® before and after contact with contaminated water.

This research has focused on the investigation of trace element removal. This was due to the expertise of the laboratory and the availability of instrumentation. However, in terms of the multi-chemical nature of the water at Cranleigh and the possible extended use of these solids, further study could focus on the removal of other elemental species (including organic forms). Whilst the conclusions propose a removal mechanism based on hydroxide ion release, it would be interesting to see if Blueguard® materials could remove PAHs, herbicides, etc.

5.2.2 Subsequent treatment

As mentioned before, it is concluded that Blueguard® materials treat the contamination in water by causing the trace elements to precipitate from the solution. Therefore, a sedimentation or filtration process (physical unit operation detailed in section 1.3.3) could be developed to separate the insoluble precipitates from water before appropriately discharged or reused (Purkayastha,
Materials that have been investigated as filter media include quartz sand, silica sand, anthracite coal, garnet and magnetite.

### 5.2.3 An operational industrialisation

Finally, in terms of the applications of Blueguard® materials on a large scale, there are a number of possible designs in which these materials may be applied. One possibility in order to remediate the chemical contamination on the site would be to construct a channel packed with Blueguard® G1-3 to which water from the leachate lagoon would be pumped through (under an optimum flow rate).
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Appendices

Appendix A Calibration Curves

Figure A-1 Calibration curve for optimisation Zn using Agilent 7700x ICP-MS

![Graph](image)

\[ y = 0.0207x \]
\[ R^2 = 0.9999 \]

Figure A-2 Calibration curve for optimisation Na using Agilent 7700x ICP-MS

![Graph](image)

\[ y = 0.0149x \]
\[ R^2 = 0.9988 \]
Appendix B  Identification of the Mineral Phases in the Materials Used in This Work

Figure B-1 X-ray diffraction profile of the material in this work and their phases, as provided by Sibelco