CHAPTER ONE: Introduction

1.1. Introduction to the thesis

Mine drainage from both metal and coal mine sites is a significant source of environmental contamination and ecological damage. The introduction of Environmental Quality Standards (EQS) and the Water Framework Directive (2000/60/EC) have meant that the remediation of polluted watercourses is becoming increasingly necessary in order to reduce contaminant concentrations to below EQS set by the European Union (EU). Research into the remediation of contaminated mine waters has generally concentrated on the treatment of ferruginous, acidic waters where the mechanisms of metal removal are well understood. However, many former mining areas of the UK are characterised by circum-neutral, low-Fe drainage with concentrations of Zn, Pb and Cd that exceed EU water quality guidelines. These circum-neutral pH, metal-rich waters present a challenging target for remediation, as the low Fe content means that simply buffering solution pH to encourage metal co-precipitation with Fe-oxyhydroxides is not a viable remediation option. A novel approach to remediation is therefore required. This thesis explores the potential for using a range of permeable reactive materials to remove selected metal contaminants (Zn, Pb and Cd) from a range of low-Fe, circum-neutral pH mine drainage waters with differing hydrochemical and geological origins.

1.2. Mine drainage in the UK

It is estimated that a total of 200km of watercourses in the UK are polluted by discharges from metal mines sites, with a further 400km being affected by discharges from abandoned coal mines (Younger, 2002). Mines currently in operation in the UK are legally required to monitor and remediate effluent discharges in order to ensure that water quality meets guidelines set by the EU. Historically, however, mining companies were not considered responsible for the environmental impact of their operations and no duty of care was in place to restore the site.
following extraction. As a result, many former mining areas of the UK are now characterised by abandoned spoil heaps and extensive underground workings, which leach grossly contaminated waters into local watercourses. This often causes them to fail EQS by up to several orders of magnitude for decades or even centuries after mining ceases.

The chemistry of mine drainage can vary significantly and is dependent upon a number of factors, including the geochemical conditions at the point source of weathering, the chemistry of the mined deposit and the nature of the host rocks and gangue minerals. As a result, mine drainage waters from different areas may be acidic and ferruginous, net alkaline and ferruginous, circum-neutral or moderate to highly saline depending upon the geochemical characteristics of the site. The chemistry of mine drainage from any given mine site is essentially the result of the competing processes of acid generation and neutralisation (Seal and Hammarstrom, 2003). In general, pyrite/marcasite-rich and carbonate-poor sites produce acidic drainage, whilst carbonate-rich sites tend to produce alkaline or circum-neutral waters, even when significant quantities of sulphide minerals are present (Ziemkiewicz et al., 2003).

1.2.1. Acid mine drainage

Until recently, attention has tended to focus on the ferruginous acidic discharges that emanate from many abandoned mine sites; so-called ‘Acid Mine Drainage’ (AMD). These waters result from the weathering of pyrite or marcasite ($\text{FeS}_2$), which are often major gangue constituents in both coal and base metal sulphide deposits. Mining activity exposes large quantities of these minerals to oxidation at the Earth’s surface, resulting in the generation of acidic waters that are rich in iron and sulphate (equations [1.1] to [1.5]). AMD formation is essentially a result of complex interacting chemical, biological and physical processes, and can be summarised by Reaction [1.1] (Nordstrom, 1982).

$$\text{FeS}_2 (s) + \frac{15}{2} \text{O}_2 (aq) + \frac{7}{2} \text{H}_2\text{O} (l) \rightarrow \text{Fe(OH)}_3 (s) + 2\text{H}_2\text{SO}_4 (aq) \quad [1.1]$$
Both atmospheric oxygen (equation [1.2]) and ferric iron (equation [1.3]) may act as oxidising agents for the pyrite (Langmuir, 1997):

\[
\begin{align*}
\text{FeS}_2 + \frac{1}{2} O_2 + H_2O &\rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2H^+ \quad [1.2] \\
\text{FeS}_2 + 14\text{Fe}^{3+} + 8H_2O &\rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16H^+ \quad [1.3]
\end{align*}
\]

Clearly the extent of acid generation is dependent upon the oxidising agent. Oxidation by atmospheric O\textsubscript{2} produces 2 moles of H\textsuperscript{+} ions from every mole of pyrite, whilst oxidation by ferric iron releases significantly more acidity, with 16 protons being released by every mole of pyrite oxidised. The ferrous iron produced by [1.2] and [1.3] is then further oxidised as follows:

\[
\begin{align*}
\text{Fe}^{2+} + \frac{1}{2} O_2 + \text{H}^+ &\rightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O} \quad [1.4] \\
\text{Fe}^{2+} + \frac{1}{2} O_2 + \frac{1}{2} \text{H}_2\text{O} &\rightarrow \text{Fe(OH)}_3 + 2\text{H}^+ \quad [1.5]
\end{align*}
\]

Oxidation of ferrous to ferric iron by reaction [1.4] is generally slow and occurs at pH values less than 3. Under these low pH conditions certain bacteria such as \textit{Thiobacillus ferrooxidans} and \textit{Acidithiobacillus ferrooxidans} may also catalyse this reaction. As partial neutralisation of the solution occurs and the pH rises above 3, oxidation of ferrous iron continues by reaction [1.5].

The low pH conditions generated by pyrite oxidation enhance the solubility of many base metals (Cu, Pb, Zn, Co, Ni, Al, Mn and Cd), hence many AMD waters are characterised by elevated concentrations of metals in solution. Iron Mountain, California, for example, represents one of the most extreme AMD sites in the world. The mine was worked for Ag, Au, Cu, Fe, Zn and pyrite between the 1860s and 1962. The deposits occur as massive sulphide lenses containing up to 95% pyrite. Periodic monitoring of drainage from the site during the period 1990 to 1991 revealed waters with negative pH values (as low as -3.6) and element concentrations in solution reaching 111,000 mg L\textsuperscript{-1} Fe, 760,000 mg L\textsuperscript{-1} SO\textsubscript{4}^2-, 9800 mg L\textsuperscript{-1} Cu, 49,300 mg L\textsuperscript{-1} Zn and 850 mg L\textsuperscript{-1} As (Nordstrom and Alpers, 1999).
Natural attenuation and neutralisation of AMD generally takes place as the drainage moves away from the point source and mixes with non-polluted waters. Weathering of carbonate and silicate minerals also help to consume acidity and buffer solution pH. This rise in solution pH results in the precipitation of iron hydroxides, oxyhydroxides and hydroxy sulphates (commonly referred to as ‘ochre’) as the pH of the water rises above the pH of iron hydrolysis. Many contaminant metals are then removed by either co-precipitation with iron or by adsorption onto the range of iron hydroxides that form as the AMD is attenuated (Dzombak and Morel, 1990).

1.2.2. Circum-neutral mine drainage

Although the term AMD is widespread in the literature, it is often misleading and does not necessarily encompass all mine drainage; it refers simply to the geochemical conditions at the point source of weathering (White, 2000). In reality, many metal-laden mine discharges are characterised by a circum-neutral pH owing to either (i) an absence of pyrite/marcasite within the ore, hence minimising the acid generating potential on site, or (ii) the presence of a carbonate host rock or gangue, which effectively neutralises any acidity produced.

The formation of circum-neutral metal mine drainage may result from the weathering of non-ferrous metal sulphides (e.g. sphalerite, galena, chalcopyrite), which release soluble metal cations into solution without the associated release of acidity (equations [1.6]-[1.8]) (Younger et al., 2002; Seal and Hammarstrom, 2003):

\[
\text{Sphalerite: } \text{ZnS}_\text{(s)} + 2\text{O}_2\text{(aq)} \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} \quad [1.6]
\]

\[
\text{Galena: } \text{PbS}_\text{(s)} + 2\text{O}_2\text{(aq)} \rightarrow \text{Pb}^{2+} + \text{SO}_4^{2-} \quad [1.7]
\]

\[
\text{Chalcopyrite: } \text{CuFeS}_2\text{(s)} + 2\text{O}_2\text{(aq)} \rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{SO}_4^{2-} \quad [1.8]
\]

In the absence of pyrite, weathering of sulphide minerals in this way results in the generation of metal-laden mine water without the generation of acidity. This results in the production of sulphate-rich and Fe-poor mine drainage waters with a circum-neutral pH. Many of these circum-neutral mine discharges are characterised by elevated concentrations of metal(loids) such as Zn, Cd, As, Mo and Se as these elements remain soluble over a wide pH range (Figure1.1).
Circum-neutral mine drainage formation may also occur from the neutralisation of AMD by carbonate and aluminosilicate minerals (e.g. Desbarats and Dirom, 2007). Many ore deposits and their associated host rocks and gangue minerals may contain one or more of the following carbonate minerals (Blowes et al., 2003):

- calcite (CaCO$_3$)
- ankerite (Ca(Fe,Mg)(CO$_3$)$_2$)
- dolomite (Ca,Mg(CO$_3$)$_2$)

Dissolution of these minerals may significantly buffer solution pH and effectively neutralise any acidity as follows:

$$\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$$  \[1.9\]

Consumption of acidity by equation [1.9] may be effective at maintaining solution pH above 5.5, resulting in the discharge of circum-neutral mine drainage waters at many mine sites. It should be noted that several aluminosilicate minerals also have the ability to buffer solution pH and consume acidity; however their associated dissolution rates are much slower than those of carbonate minerals, and they are therefore usually less significant in the neutralisation of acidic mine waters.
Many former mining areas of the UK are characterised by metal-laden, circum-neutral pH drainage owing to either a lack of pyrite within the ore body or the neutralisation of acidity by the dissolution of carbonate and aluminosilicate minerals. For example many of the mines in the limestone-hosted former Pb-Zn mining area of the North Pennines have net-alkaline drainage waters with high CaCO$_3$ contents and elevated concentrations of Cd, Pb, As and Zn ($\leq 40$ mg L$^{-1}$) (Younger, 2000). Similarly, many of the abandoned base metal mines in the mid-Wales Orefield are characterised by circum-neutral drainage waters as a result of the low pyrite content of the ore (Hartley, 2009).

1.2.3. Metal contaminants in circum-neutral mine waters

Many of the circum-neutral mine discharges in the UK are located in areas with hydrothermal base metal sulphide deposits which are often pyrite-poor. For this reason, the contaminants that are likely to be present in the drainage include Zn, Pb, Cd, As, Cr and Ni. Iron is unlikely to be present in significant quantities, and Fe concentrations in areas with circum-neutral metal mine drainage rarely exceed 0.5 mg L$^{-1}$ (Hartley, 2009). Many of the metal cations likely to be present in circum-neutral mine waters are known to be toxic to humans and/or aquatic organisms if present in elevated concentrations. For example Earle and Callaghan (1998) recognise the toxic effects of elements such as Zn and Cd to aquatic life, even at very low concentrations. This study focuses on Zn, Pb and Cd as these are considered to be the primary target contaminants in circum-neutral mine waters. A brief overview of the geochemical behaviour of these elements in natural, aqueous environments is given below, together with the potential health effects on organisms if present in toxic quantities.

1.2.3.1. Zinc

Zinc is the 23rd most abundant element in the Earth’s crust and is the primary constituent of the ore mineral sphalerite (ZnS). It is present in most natural waters at concentrations of 10 µg L$^{-1}$ or less (Hem, 1992); however concentrations may be several orders of magnitude higher in drainage waters from abandoned Pb and Zn mines. In aqueous systems Zn is fairly soluble over a wide pH range and may be
present as the free Zn ion (Zn$^{2+}$) (pH ≤7.5) or associated with sulphide, carbonate or oxide complexes (at pH >7.5) (Figure 1.2). For this reason, Zn is a common contaminant in many circum-neutral mine drainage waters, and is notoriously difficult to remove from solution (Nuttall and Younger, 2000). As such, it is considered to be the primary metal ion of interest in this study.

Figure 1.2: Eh-pH diagram showing the predominant dissolved Zn species in the system Zn + CO$_2$ + S + H$_2$O at 25°C and 1 atm pressure. Dissolved Zn activity = 10$^{-5}$ moles L$^{-1}$. Dissolved CO$_2$ and S activity = 10$^{-3}$ moles L$^{-1}$ (Hem, 1972).

In trace quantities, Zn is considered an essential element in both human and animal health. However, there are also reported cases of Zn toxicity, whereby elevated exposure has led to diarrhoea, vomiting, pulmonary distress and gastroenteritis (WHO, 2003a). Excessive Zn exposure may also result in copper deficiency, as Zn is known to interfere with Cu metabolism within the body. Zinc is highly ecotoxic in the aquatic environment and is known to affect freshwater biology in mining areas (Kelly, 1988). The toxicity of Zn to aquatic organisms is also thought to be affected by both solution pH and hardness. For example rainbow trout have shown to be more sensitive to high Zn concentrations at circum-neutral pH (Hansen et al., 2002). Similarly, Zn is known to be more toxic in low hardness waters (Table 1.1).
1.2.3.2. Cadmium

Cadmium is geochemically very similar to Zn and therefore tends to occur naturally with Zn and Pb in sulphide ores. Unpolluted surface waters generally contain \(<1 \mu g \text{ L}^{-1}\) (Hem, 1992), however this may rise significantly in areas around sulphide mineralisation or mining activity. Cadmium in surface waters is generally present as the free Cd\(^{2+}\) ion, which is soluble up to pH 8.3 (Hem, 1972) (Figure 1.3). As a result, Cd is a common constituent of circum-neutral pH drainage waters.

![Figure 1.3: Eh-pH diagram showing the predominant dissolved Cd species in the system Cd + CO\(_2\) + S + H\(_2\)O at 25\(^\circ\)C and at 1 atm pressure. Dissolved Zn activity = 10\(^{-7.05}\) moles L\(^{-1}\). Dissolved CO\(_2\) and S activity = 10\(^{-3}\) moles L\(^{-1}\) (Hem, 1972).](image)

Cadmium is considered to be extremely ecotoxic, and elevated exposure is known to cause kidney damage (Herber et al., 1988), renal degradation, skeletal deformity (Mohan and Singh, 2002) and affect fertility in humans (Kumar et al., 2000). Cases of elevated exposure to Cd in drinking water in Japan have led to the development of itai-itai disease (osteoporosis accompanied by severe renal tubular disease) (WHO, 2004). As a result, Cd is listed as a priority contaminant under the EU Water Framework Directive (2000/60/EC), which sets the imperative standard for Cd in surface waters at 1 \(\mu g \text{ L}^{-1}\).
1.2.3.3. Lead

Lead is the most abundant heavy element in the Earth’s crust. It is commonly found associated with base metal sulphide deposits as galena (PbS), and may be enriched in soils, waters and vegetation around historical mining areas. In the majority of natural waters Pb is present in very low concentrations owing to its low solubility and strong tendency to sorb onto inorganic sediments (Hem, 1992). For example average Pb concentrations in unmineralised streams in North Wales were approximately 0.5 \(\mu g\) L\(^{-1}\) (Kelly, 1988). Where Pb is present in significant quantities, it tends to be present as the free Pb\(^{2+}\) ion at pH values <7.1. Above this, Pb tends to form carbonate and hydroxide complexes (Kelly, 1988). Lead has no known nutritional biochemical or physiological function and is considered a toxic metal to humans, aquatic fauna and livestock. Exposure to elevated concentrations of Pb in humans has proven to affect neuro-psychological development and behaviour in infants (Wigg, 2001; Gordon et al., 2002). High aquatic Pb concentrations are also known to affect the health of freshwater fish, especially salmon and trout. For example Carpenter (1924) surveyed the rivers in the mining districts of Ceredigion, mid-Wales and concluded that significant concentrations of Pb in solution were causing the formation of mucus on fish gills, which was effectively suffocating the fish. As a result, Pb and its compounds are listed as priority substances under the Water Framework Directive. This legislation sets the imperative guideline for Pb at 50 \(\mu g\) L\(^{-1}\).

1.3. Water quality standards

The increasing recognition of water pollution by agricultural, mining and industrial activities has led the EU to develop and implement of a number of Directives that regulate and control water quality in Europe. The most significant of these are detailed below.

1.3.1. Dangerous Substances Directive (76/464/EEC): This was one of the first acts of water quality legislation to be introduced in 1976. The Directive is primarily related to the discharge of organic and inorganic
pollutants to inland surface waters, terrestrial waters, inland coastal
(estuarine) waters and groundwater. Under the Dangerous Substances
Directive, pollutants may be listed under either List I or List II; the
directive aims to eliminate List I substances and minimise the presence of
List II substances in surface waters. List I pollutants (e.g. Cd) are
generally considered particularly toxic and bioaccumulate in the
environment. List II substances (e.g. Pb and Zn) are considered to have
‘…a deleterious effect on the aquatic environment’. Since its introduction,
there have been a number of changes to Directive 76/464/EEC, and the
eventual aim is to fully incorporate it into the Water Framework Directive.

1.3.2. Freshwater Fish Directive (78/659/EEC): This Directive aims to
protect water bodies that have been identified as having sustainable fish
populations. Under the Freshwater Fish Directive, water bodies are
classified as either salmonid (containing salmon or trout) or cyprinid
(containing, carp, tench or roach). The Directive sets both guideline (‘G’)
and imperative (‘I’) standards for a number of physical and chemical
water parameters. Of the substances listed under Directive 78/659/EEC,
Zn is of most significance to this study. Imperative water quality
standards for Zn in salmonid rivers vary between 0.03 and 0.5 mg L\(^{-1}\)
depending on water hardness. Imperative water quality standards are
more stringent in lower hardness waters as a result of the increased
toxicity of metal contaminants under these conditions.

covers the collection, treatment and discharge of urban waste waters from
homes and industry. It also is particularly concerned with the discharge
and treatment of water from industrial sectors. Environmental quality
standards set by the Urban Wastewater Treatment Directive are mainly
for biological parameters, including BOD and COD. Suspended solids,
total nitrogen and nitrates are also monitored under the Directive.

1.3.4. Water Framework Directive (WFD) (2000/60/EC): This act of
legislation came into force in the year 2000 and will be gradually
implemented over the next 25 years. The Directive aims to improve and integrate the way that water bodies are managed throughout Europe. One of the primary objectives of the WFD is to promote the sustainable use of water and to reduce the pollution of water bodies (lakes, rivers, coastal waters and groundwaters), particularly by ‘priority’ substances. It was aimed that by 2007 the Water Framework Directive would have gradually been incorporated and would have repealed a number of previous Directives, including the Freshwater Fish Directive (78/659/EEC) and the Dangerous Substances List (76/464/EEC). It should be noted that List I substances (including Cd) under the Dangerous Substances List (76/464/EEC) have now been reclassified as ‘Priority Substances’ under the WFD. List II substances will remain the same until 2013, when they will be fully incorporated into the WFD. Directive 2000/60/EC stipulates that all UK inland and coastal waters should reach “good status” by 2015.

Clearly the legislation governing water quality in surface, coastal and groundwaters is complex. Although the introduction of the WFD (2000/60/EC) aimed to simplify and integrate water pollution control throughout Europe, there is still no single set of water quality standards that can be applied to all surface (non-drinking) waters. The most comprehensive list of pollutants is given under the Dangerous Substances Directive (76/464/EEC), which lists both imperative and guide values for salmonid and cyprinid water bodies. This list is gradually being incorporated into the WFD, and will therefore be employed as the primary set of water quality standards throughout this project. Imperative water quality standards under Directive 76/464/EEC for Zn, Pb and Cd (the primary contaminants in circum-neutral mine drainage waters) are given in Table 1.1.
Table 1.1: Imperative water quality standards for selected contaminants under List II of EU Directives 76/464/EEC and 2006/11/EC

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fraction</th>
<th>Imperative water quality standard (µg L⁻¹)</th>
<th>Notes¹</th>
</tr>
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<tbody>
<tr>
<td>Cd</td>
<td>Total</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>Dissolved</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>Pb</td>
<td>Dissolved</td>
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<td>Hardness: 0-50</td>
</tr>
<tr>
<td></td>
<td>Dissolved</td>
<td>10</td>
<td>Hardness: 50-150</td>
</tr>
<tr>
<td></td>
<td>Dissolved</td>
<td>20</td>
<td>Hardness: &gt;150</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>6-9</td>
<td>-</td>
</tr>
<tr>
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<td>Total</td>
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<td>Hardness: 0-50</td>
</tr>
<tr>
<td></td>
<td>Total</td>
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</tr>
<tr>
<td></td>
<td>Total</td>
<td>75</td>
<td>Hardness: 100-250</td>
</tr>
</tbody>
</table>

¹Hardness values are in mg L⁻¹ as CaCO₃

1.4. Mine water remediation

1.4.1. Active treatment of mine waters

The introduction of water quality guidelines and the EU Water Framework Directive have meant that remediation of polluted watercourses is becoming increasingly necessary in order to reduce contaminant concentrations to within legal guidelines. Mines currently in operation often have expensive active treatment plants in place to treat effluent discharges before release into local watercourses. These ‘active’ treatment methods generally involve the addition of a chemical neutralising agent to raise solution pH, accelerate the oxidation of ferrous iron and encourage the precipitation of metals as hydroxides and carbonates (Johnson and Hallberg, 2005).

One of the most commonly-used active treatment methods involves oxidation and alkali-dosing, followed by the flocculation and sedimentation of suspended solids. This is generally sufficient to reduce concentrations of Fe, Zn, Cu, Al and Cd to within acceptable guidelines as follows:

(a) Oxidation: This step is carried out primarily to oxidise all Fe²⁺ and Mn²⁺ in solution and convert them to a less soluble form (i.e. Fe³⁺ and Mn⁴⁺)
(b) Alkali-dosing: Addition of a chemical neutralising agent (e.g. lime, calcium carbonate, sodium carbonate, sodium hydroxide, magnesium hydroxide) increases solution pH to around 6.5 – 8.5. This promotes precipitation of Fe hydroxides, and Zn, Ni, Pb, Cd and Mn hydroxides may also be encouraged to precipitate if pH is raised significantly.

(c) Flocculation/sedimentation: This stage of active treatment allows any suspended solids to settle from suspension and be effectively removed.

This process produces large quantities of low-density, iron-rich sludge, which is difficult to handle. It is commonly disposed of in landfill or recycled, although the wider environmental costs of waste sludge disposal are often significant.

Active treatment plants have a number of shortcomings, primarily owing to their constant monitoring requirements and large energy and chemical inputs. As a result, active mine water treatment is commonly an expensive process. In spite of these shortcomings, active treatment plants have the advantage that effluent water quality can be precisely controlled and monitored. The plants are also able to cope with significant variations in influent water chemistry, as the quantities of reagents added during treatment can be altered accordingly.

1.4.2. Passive treatment of mine waters

It is generally considered unsuitable to take an active approach to mine water remediation at abandoned mine sites in the UK and Ireland, for a number of reasons. Firstly, it was typical of mine owners to relinquish responsibility on site when extraction ceased, therefore assigning the costs associated with remediation is difficult and the responsibility often falls on bodies such as the Environment Agency to ensure that water quality remains within Environmental Quality Standards. Consequently any remedial action undertaken on historical mine sites must generally have relatively low associated operating and maintenance costs. Secondly, many of the most polluting abandoned metal mine sites are located in remote areas with limited access and transport connections. This makes active remediation technologies such as pump-and-treat systems prohibitive in terms of both cost and practicality (Naftz et al., 2002). As a result, so-called ‘passive’ treatment systems
with minimal operating and maintenance requirements have emerged as an attractive alternative remediation technology over the past 20 years. Passive treatment has been defined by Younger et al. (2002) as:

‘...the deliberate improvement of water quality using only naturally-available energy sources (e.g. gravity, microbial metabolic energy, photosynthesis) in systems which require only infrequent (albeit regular) maintenance in order to operate effectively over the entire system design life.’

To date, passive treatment systems have been particularly popular in the Eastern United States, where the topography and land availability are favourable. Construction of such systems in the UK has proved more problematic as a result of the location of many mine sites in areas with steep sided valleys or limited land availability. Nevertheless, passive treatment systems have been widely used in the UK to treat coal mine drainage and have also had some application for the treatment of metalliferous mine discharges.

At present, several methods of passive water treatment are in use in the UK, including aerobic wetlands, anaerobic compost wetlands, Reducing-and-Alkalinity-Producing Systems (RAPS), limestone filter beds and subsurface reactive barriers. It is estimated that at least 38 full-scale passive treatment systems are currently in operation in the UK (Coal Authority, 2009). The majority of these passive treatment plants treat acidic, ferruginous waters at abandoned coal and metal mine sites, where the mechanisms of metal removal are well understood. In general, passive treatment of such acidic mine drainage requires processes that (i) raise pH and reduce contaminant mobility, (ii) alter the redox conditions of the water, thereby reducing the solubility of contaminant metals and (iii) raise the solution pH above the pH of Fe hydrolysis in order to encourage the precipitation of Fe and subsequent co-precipitation/sorption of contaminant metal ions onto Fe (oxy)hydroxide precipitates. Most passive treatment systems for acidic discharges generally have an acid-neutralising or an alkalinity-generating source in order to raise solution pH. Alternatively, many other AMD treatment systems rely on sulphate reduction under anoxic conditions, which promotes the precipitation of insoluble metal sulphides and
effectively removes them from solution. Nevertheless, the chemical mechanisms behind acid mine drainage remediation are well understood and as a result there is a large number of passive treatment systems in place for the treatment of acidic-ferruginous waters. A brief overview of the major passive treatment technologies (normally used for the remediation of acidic, ferruginous mine drainage) is given below.

1.4.2.1. Anoxic limestone drains

Anoxic limestone drains (ALDs) are relatively simple systems, which are purely designed to raise solution pH and are often used as a pre-treatment stage in passive treatment systems. They are essentially sealed cells containing a limestone substrate, which generates alkalinity by carbonate dissolution. The anoxic nature of ALDs means that release of CO$_2$ from the system is not possible, resulting in a build-up of bicarbonate which serves to further increase solution pH. The anoxic conditions within the ALD and the ‘closed’ nature of the system also allow Fe, Al and Mn to remain in their reduced states (Younger et al., 2002). This prevents the precipitation of these metals and hence ensures that a loss in system reactivity is not observed by ‘armouring’ of the limestone by metal hydroxides. ALDs are generally considered unsuitable for the treatment of waters containing over 1 mg L$^{-1}$ of dissolved O$_2$, Fe$^{3+}$ and Al$^{3+}$.

1.4.2.2. Oxic limestone drains (OLDs)

Oxic limestone drains are similar in their design to ALDs, however the system differs in the fact that it is open to atmospheric O$_2$ and therefore Fe and Al hydroxides are allowed to precipitate. Oxic limestone drains also have the advantage that they are able to effectively treat waters containing over 1 mg L$^{-1}$ of Al, Mn and Fe. Maintenance of high flow velocities within the system keeps any precipitated hydroxides in suspension and prevents armouring of the limestone. Suspended solids are then allowed to settle in wetlands once the fluid has left the OLD system. Oxic limestone drains have proved successful in generating alkalinity and raising pH with only a 2-3 hour residence time (Younger et al., 2002).
1.4.2.3. Reducing and alkalinity producing systems (RAPS)

RAPS were originally designed to overcome some of the shortcomings of ALDs (i.e. their ability to only treat waters containing less than 1 mg L\(^{-1}\) Al\(^{3+}\), Fe\(^{3+}\) and O\(_2\)). RAPS are essentially composed of a limestone substrate overlain by a compost bed (Figure 1.4).

![Figure 1.4: Schematic of a Reducing and Alkalinity Producing System (RAPS) (adapted from Younger et al., 2002).](image)

The water flows into the top of the system, first contacting with the compost which generates a reducing environment. Subsequent contact with the limestone then generates alkalinity and raises solution pH. The reducing nature of the system has the advantage that armouring of the limestone is avoided and that metals can be effectively removed by precipitation as sulphides. RAPS are generally considered to be more efficient than wetlands and have smaller land requirements, as the water is forced to be in contact with both the limestone and compost for a minimum 14 hour retention time (Younger et al., 2002).

1.4.2.4. Aerobic wetlands

Wetlands were one of the first passive treatment systems to become established in the USA during the 1970s. They have proven particularly effective at treating net-alkaline, Fe-rich mine waters, and their low running costs make them an attractive option for remediation. Aerobic wetlands are designed to promote the oxidation and hydrolysis of Fe, Al and Mn, and are generally composed of wetland vegetation (e.g. *Typha* or *Juncus*) in a shallow substrate (Ziemkiewicz et al., 2003). Iron is removed by a combination of (i) settlement of Fe-hydroxides from solution (ii) metal uptake by plants (iii) filtering of suspended material and (iv) formation of Fe
oxide/hydroxide precipitates (Younger et al., 2002). Aerobic wetlands are generally not considered suitable for the treatment of acidic mine waters, as the oxidation of Fe$^{3+}$ and Al$^{3+}$ within the system releases H$^+$ ions into solution which serves to further increase acidity. However, aerobic systems have proven effective at treating net-alkaline, ferruginous waters.

1.4.2.5. Compost wetlands

Compost wetlands differ from aerobic wetlands by their thick (≤0.5m) organic substrate, which promotes sulphate reduction by sulphate reducing bacteria (SRB). The bacteria use sulphate to oxidise the organic matter within the wetland, with H$_2$S and HCO$_3^-$ being released as bi-products of this reaction. The bicarbonate produced by this process serves to increase solution pH, whilst the hydrogen sulphide reacts with metals in solution resulting in the precipitation of insoluble metal sulphides (reaction [1.10]) (Gazea et al., 1996):

$$\text{Me}^{2+} + \text{H}_2\text{S} \rightarrow \text{MeS} + 2\text{H}^+ \quad [1.10]$$

Compost wetlands are designed for the treatment of net acidic mine water, with metal removal occurring by a combination of sulphide, hydroxide and carbonate precipitation. A variety of organic materials have been used as substrates in compost wetlands, including spent mushroom compost (Hedin et al., 1994), peat, cow/horse manure, bark, mulch, sawdust and paper-making waste.

1.4.2.6. Permeable Reactive Barriers (PRBs)

Permeable Reactive Barriers (PRBs) are engineered walls of reactive materials that are installed in a trench in the path of a contaminant plume to both control the rate of groundwater flow and to provide in-situ remediation of contaminants. PRB technology relies on natural groundwater gradients to move the contaminant plume through the zone of reactive materials (Morrison et al., 2002). Contaminants are removed by either adsorption onto the surface of the reactive material or by a combination of chemical, physical and biological reactions, which promote precipitation or stabilisation of contaminants. To date a range of reactive materials
have been successfully used to treat a number of inorganic metal/metalloid contaminants (Co, As, Cr, Zn, Pb, Ni) in PRB systems. These include Zero Valant Iron (ZVI) (Blowes et al., 1997; McRae et al., 1999; Morrison et al., 2002; Naftz et al., 2002), activated carbon (Leinonen and Lehto, 2001), activated alumina, apatite (Fuller et al., 2002), municipal compost mixtures (Gibert et al., 2005a), wood chips (Waybrant et al., 2002; Gibert et al., 2003), peat (Crist et al., 1996), clay minerals (Kaya and Ören, 2005), limestone and zeolites (Hui et al., 2005). Ideally, PRBs should reduce contaminant concentrations to acceptable concentrations whilst retaining adequate permeability and reactivity over extended time periods. PRB design is tailored to individual sites depending upon the prevailing hydrochemical and geological conditions. Hence there is great potential to adapt PRBs to treat waters at a wide range of sites.

### 1.5. Remediation of circum-neutral mine waters

The passive treatment systems described in detail in section 1.4.2. are all designed to treat mine waters with varying chemical characteristics. Selection of the most appropriate passive treatment system for any given site is undoubtedly dependent upon the hydrochemistry, flow rates and topography. At present, the majority of passive treatment systems are designed to treat acidic and/or Fe-/Al- and Mn-rich waters (Ziemkiewicz et al., 2003), whereby treatment may be aided by high concentrations of Fe in solution. Treatment of these waters may involve simply buffering the pH to above the pH of Fe hydrolysis, effectively removing metal contaminants by co-precipitation with Fe-oxyhydroxides. Subsequent metal removal may then occur by adsorption of metal cations onto the Fe-hydroxides and oxyhydroxides that form during this process (Johnson, 1986; Dinelli and Tateo, 2002).

Although considerable research has been conducted into the remediation of AMD waters, little attention has been paid to the remediation of low-Fe and/or circum-neutral metal mine drainage. Treatment of such waters is difficult, as precipitation of metal sulphides does not readily occur at circum-neutral pH values and the low Fe content of many of these waters also means that remediation is not aided by the co-
precipitation of metals with Fe (oxy)hydroxides above the pH of Fe hydrolysis. As a result, these waters present a challenging target for remediation.

Encouragingly, many studies have shown that mine water remediation is strongly dependent on solution pH, with metal removal (particularly by adsorption) being more effective at circum-neutral pH values (Dzombak and Morel, 1990; Chen et al., 1997; Edyvean et al., 1997; Scherer et al., 2000). For example many metal cations such as Pb, Cu, Zn and Cd have been shown to sorb more strongly at circum-neutral to moderately alkaline pH values (Figure 1.5). In addition, the performance of many previously-used PRB reactive materials has shown to be strongly affected by solution pH. For example the sorption of metals onto activated carbon and peat has shown to be most effective at circum-neutral to slightly acidic pH (Corapcioglu and Huang, 1987; Crist et al., 1996). Similarly, metal sorption onto clays and calcite (Ettler et al., 2006) has shown to be strongly pH-dependent, with increased amounts of sorption occurring at higher pH values. For these reasons, there may be the potential to use many of these permeable reactive materials in the remediation of metal-laden, circum-neutral mine drainage waters.

Figure 1.5: (a) Model sorption curves showing the sorption of selected metals onto hydrous ferric oxide (HFO) (Dzombak and Morel, 1990) (b) pH-dependent metal cation/anion adsorption onto calcium carbonate (Zachara et al., 1991)
1.6. Aims of the project

The primary aims of the thesis are outlined below:

(i) To determine whether a selected range of permeable reactive materials can be used to effectively remove metal contaminants (primarily Zn, Pb and Cd) from circum-neutral, low-Fe mine drainage waters on a laboratory-scale.

(ii) To determine the effect that mine water hydrochemistry (primarily pH, Fe, Ca, Mg) has on treatment efficiency.

(iii) To compare metal removal rates and patterns between selected circum-neutral and acid mine drainage waters using laboratory batch experiments.

(iv) To determine the longevity of systems receiving circum-neutral mine drainage using long-term laboratory column investigations.

(v) To assess how mine water hydrochemistry could potentially affect the size of full-scale passive treatment systems in areas with circum-neutral mine drainage.

(vi) To determine the role that geochemical modelling plays in predicting and/or interpreting metal removal patterns.

1.7. Permeable Reactive Barrier technology

Permeable Reactive Barriers have gained popularity in recent years owing to their ability to treat a range of organic and inorganic contaminants with minimal operating and maintenance costs. This makes them an attractive option for the remediation of metal-contaminated waste waters (Robertson et al., 2005). PRBs have been known under various acronyms since they were first introduced in the early 1990s, including chemical barriers (Spangler and Morrison, 1991), permeable reactive walls (Blowes and Ptacek, 1992; O’Hannesin and Gillham, 1993) and porous reactive walls (Blowes et al., 1997). However, Permeable Reactive Barrier is now the most widely accepted terminology.
PRBs offer a significant advantage over many passive treatment technologies, as they are commonly installed in a trench, and therefore have minimal land requirements and do not demand significant above-ground infrastructure. The installation of reactive materials within a trench means that the overlying land may be landscaped, with only intermittent monitoring wells being required at the surface. This is an extremely desirable characteristic for remediation, as many conventional passive treatment technologies (primarily wetlands) have large land requirements, which is a major obstacle in the UK where the high cost of land and the topography are major limitations. For example Wheal Jane Passive treatment system in Cornwall has land requirements of 12,000 m$^2$, and yet the system only treats 2% of the total drainage emanating from the abandoned Sn/Zn mine (Younger et al., 2005). This can be compared to Fry Canyon PRB system, Utah, which consists of 3 PRB ‘gates’, each only 2.1 x 0.9 metres in size (Naftz et al., 2002).

Throughout the 1990s, the state of PRB technology has developed significantly from laboratory-scale studies to full-scale applications. The first example of a field-scale PRB was installed in 1991 at Canadian Forces Base Borden, Ontario, which used zero valent iron (ZVI) to treat Trichloroethylene (TCE) and Perchloroethylene (PCE) (Gillham and O’Hannesin, 1994). The success of this system led to the design and installation of several tens of PRB systems to treat both organic and inorganic contaminants using a range of reactive materials. At present, the majority of full-scale PRBs in operation are located in the USA where there is a greater reliance on groundwater for drinking water supply, although there are currently an estimated 10 PRBs in operation in the UK (Younger, 2003). The first full-scale PRB in the UK was installed at Shilbottle in Northumberland to treat a ferruginous, metal-rich spoil discharge (Jarvis et al., 2006). Waters draining from the site exceed the Environment Agency Environmental Quality Standards by several orders of magnitude for Fe, Mn and Al. As a result, a PRB consisting 25% green waste compost, 25% composted horse manure and 50% limestone gravel was installed at the site in May 2003 at an initial cost of £60,000. The first 2 years of monitoring data have shown that the barrier system was effective at removing substantial quantities of Fe, SO$_4^{2-}$, and Al with low maintenance costs (<£5000 p.a.). However, the relatively new nature of the technology means that there is generally a limited amount of monitoring data on the long-term performance and efficiency of PRBs.
1.7.1. Metal removal mechanisms

Metal removal in PRBs generally occurs through a combination of reduction, chemical precipitation and adsorption, but is dependent on the contaminant and the reactive material used. Morrison et al. (2002) recognise that there are five main contaminant uptake mechanisms in PRBs:

(a) Biotic reduction – This is the most common metal removal mechanism in organic-based PRBs used to treat metals, sulphate and nitrate. The organic material within the PRB (commonly compost, peat or leaf mulch) serves as an electron donor, and contaminants are subsequently removed by reductive precipitation. The development of sulphate-reducing bacteria plays a significant role in metal removal by biotic reduction.

(b) Abiotic reduction – This is most common in ZVI-based PRB systems, whereby a low oxidation potential is generated forcing the precipitation of low solubility, redox-sensitive contaminants such as As, U and Cr.

(c) Chemical precipitation – Metal removal by chemical precipitation is common in PRBs treating AMD. In these systems limestone is used to buffer groundwater pH, and the subsequent rise in alkalinity promotes hydroxide precipitation.

(d) Adsorption – Adsorption is one of the most common mechanisms of contaminant removal in PRBs, and describes the association of metal ions with the surface of the reactive material via electrostatic interactions (Scherer et al., 2000). Adsorption reactions occur rapidly and are generally reversible (Morrison et al., 2002). They are common mechanisms of metal removal within PRBs, as many reactive materials have a net-negative surface charge (e.g. clays and compost). This creates a strong electrochemical attraction for positively charged metal cations in solution and metals are effectively held on the surface of the reactive material.
Ion exchange - Ion exchange reactions are common in zeolite and peat PRBs, whereby major cations (Ca, Mg, K, Na) in the reactive material structure substitute for metal cations in solution.

1.7.2. Permeable Reactive Barrier design

In 2002 the Environment Agency released general practise guidelines for the design and implementation of PRBs in the UK (Environment Agency, 2002a). These included information on screening studies, PRB construction and operation, performance monitoring and decommissioning. The PRB design process is complex and requires consideration of site-specific factors, including geology, host rock permeability, groundwater hydrochemistry and pH and the contaminant of interest. As a result, PRBs are generally tailored to individual sites and the design process can therefore represent a significant portion of the total cost associated with PRB installation.

1.7.3. Review of potential reactive materials for use in Permeable Reactive Barriers

Selection of the appropriate permeable reactive material is clearly a critical step in the design of a PRB system, and is primarily dependent upon the target contaminant and the chemistry of the water. Many reactive materials are now widely recognised as effective treatment materials for certain contaminants; however, it may also be necessary to use mixtures of reactive materials in order to successfully treat multi-contaminant waste plumes. In general potential reactive materials must possess a number of characteristics in order to be considered suitable for use in a PRB. Scherer et al. (2000) recognise that reactive materials must immobilise contaminants at a sufficiently rapid rate whilst maintaining adequate permeability and reactivity over extended time periods. Appropriate reactive materials should also not release any harmful compounds into the water stream down gradient of the PRB as a result of treatment. In order to keep remediation costs to a minimum, the chosen materials should be readily available in multiple-tonne quantities at a fairly low cost and preferably be produced in close proximity to the target site. Reaction time and the speed of metal uptake will play an important role in the selection of materials for use
in PRBs. For example engineers will better favour materials showing a rapid uptake of metals in a short time period than those that require a longer period for metal sorption to occur. This will ensure shorter residence times within the PRB and also has important implications for the size of the passive treatment system.

The need for readily available, inexpensive reactive materials for use in passive treatment systems such as PRBs has led research into considering a wide range of potential media. At present, research is beginning to focus on low-cost industrial by-products, which could possibly be used as reactive materials in PRBs (e.g. Bailey et al., 1999; Lee et al., 2004). Such low-cost sorbents include zeolites (Hui et al., 2005), peat and peat moss (Crist et al., 1996), chitin, seaweeds and their derivatives, activated carbons (Leinonen and Lehto, 2001), rice hulls (Said et al., 1992) bark (Masri et al., 1974), fly ash (Wantanaphong et al., 2004), iron-oxide coated sands (Stahl and James, 1991), compost (Gibert et al., 2005a,b) sawdust (Dikshit, 1989) and clays (Kaya and Ören, 2005). These materials have all been recognised as being readily available at a fairly low cost and have been shown to have metal-sorptive properties. Many of them are also available as waste products from industrial or agricultural processes, and are therefore available in large quantities.

Permeable reactive materials, which have been successfully used to treat a range of metal contaminants in the UK and the USA are described below. The potential of these materials to treat circum-neutral mine drainage waters will also be considered.

1.7.3.1. Zero-valent iron (ZVI)

Zero valent iron (ZVI or \( \text{Fe}^0 \)) is a scrap metal product that is a by-product of the automotive industry and is the most commonly used material in PRBs. It has been used to successfully treat a variety of waters containing radionuclides, organic and inorganic contaminants including benzene (Plagentz et al., 2006), chlorinated ethanes (Dries et al., 2005; Plagentz et al., 2006), U (Morrison et al., 2006; Noubactep et al., 2005), As (Bang et al., 2005; Kanel et al., 2005; Leupin and Hug, 2005; Su and Puls, 2001; Zhang et al., 2005), Mo (Morrison et al., 2006; Zhang et al., 2005), Cr (Kaplan and Gilmore, 2004; Wilkin et al., 2005) and other metals including Zn, Al, Ni, Cu and Cd (Shokes and Möller, 1999). The first ZVI-based
PRB was installed to treat chlorinated organic solvents at the Canadian Forces Base Borden site in Ontario, Canada in 1991 (Gillham and O’Hannesin 1994). The success of this system led to the installation of many more ZVI PRBs to treat organic contaminants and prompted research into the use of ZVI to treat a range of inorganic contaminants, such as Cr(VI) and As.

ZVI represents an effective, low-cost reactive material for the degradation of a number of contaminants. Metal removal is thought to occur by a combination of reductive precipitation and metal adsorption, with the ZVI acting as an electron donor (Gu et al., 2002; Rowland, 2002; Blowes et al., 2003). Corrosion of ZVI within the barrier system buffers groundwater pH and creates strongly reducing, oxygen depleted and alkaline conditions (Rowland, 2002). These provide ideal conditions for sulphate reducing bacteria (SRB) to thrive, and the $S^{2-}$ produced by this reacts readily with metal cations (Cd, Cu, Ni, Pb and Zn) in solution to form sparingly soluble sulphide compounds. Significant metal removal is also thought to take place by the sorption of metal contaminants onto Fe (oxy)hydroxides, which are secondary corrosion products formed by the oxidation of ZVI.

ZVI has been conventionally been used to treat acid mine drainage, as the corrosion of ZVI produces OH$^{-}$ ions under both aerobic and anaerobic conditions. This effectively raises solution pH, with 2 moles of OH$^{-}$ being produced for every mole of Fe$^{0}$ oxidised (Gu et al., 1999). However, research into the ability of ZVI to treat circum-neutral and Ca-rich mine drainage waters is limited. Because the sorption of metal contaminants onto secondary Fe (oxy)hydroxide corrosion products represents the major contaminant removal mechanism by ZVI, it is possible that the material may be ideally suited to remove Zn, Pb and Cd from circum-neutral pH mine waters. This is because metal sorption onto HFO has shown to increase at higher pH values (Figure 1.5(a)), meaning that potentially much higher levels of metal removal could be achieved in circum-neutral pH mine waters compared to AMD waters. One of the primary examples of a full-scale ZVI PRB treating circum-neutral (pH 6.8) metal mine drainage has so far proved effective. The system was installed at the Monticello former U processing site, Utah in June 1999 and was designed to treat groundwater contaminated with As, Mo, NO$_3$-, Se, U and V (Morrison et al., 2002). Performance monitoring during the first 16 months of PRB operation show that there was over
98% removal of U, V, As and Se. This provides encouraging results for the potential use of ZVI for the treatment of further circum-neutral mine waters.

1.7.3.2. Activated carbon

Carbon is one of the earliest-used sorbents in water treatment, with references to its use dating back to 1500BC (Wase and Forster, 1997). Charcoal was used as a water purifier in the 19th Century when highly polluted water from the River Thames was frequently treated by filtering through charcoal prior to use (McKay and Allen, 1997). Activated carbon is the most commonly used carbon sorbent, and is created by heating a source of charred organic carbon (e.g. rice hulls, coconut shells, peat) to a sufficiently high temperature (approximately 900°C) in order to cause burn-off of non-carbon impurities (Mattson and Mark, 1971). Oxidation of the material following heating then ensures the yield of an ‘active’ product. Commercially, activated carbons have been created from a wide-range of carbonaceous starting products including rice hulls, peat, coal, coconut shells, sawdust and wood char. Although activated carbon has been used as a water purifier for centuries, it is only since the 1920s that it has received considerable attention as a potential adsorbent. Bartell and Miller (1922) were the first to carry out a series of experiments studying electrolyte adsorption onto activated carbon (Mattson and Mark, 1971). A number of subsequent studies have demonstrated that the highly porous nature of activated carbon (Figure 1.6) and hence its high surface area makes it an effective sorbent for metal ions (Netzer and Hughes, 1984; Corapcioglu and Huang, 1987; Gabaldón et al., 1996).

Figure 1.6: SEM image depicting porous nature of activated carbon (x 1000 magnification)
Activated carbon was commonly used for the removal of organic contaminants from industrial wastewaters and was rarely used for the treatment of inorganic pollutants. However, studies by Netzer and Hughes (1984) and Gabaldón et al. (1996) during the late 1980s have demonstrated the ability of activated carbon to remove significant quantities of Cu, Pb, Cd and Zn from wastewaters. Metal removal is thought to occur as a result of electrostatic forces between the ionic species in solution and the surface of the reactive material, with the maximum adsorption occurring at circum-neutral to moderately acidic pH (3-6) (Corapcioglu and Huang, 1987). For this reason, it could potentially be used as a reactive material for the remediation of metal-rich, circum-neutral mine waters.

1.7.3.3. Carbonate minerals

Carbonate materials such as limestone and calcite have frequently been used to neutralise acid mine drainage in passive treatment systems (Hedin et al., 1994). For example many AMD treatment systems such as anoxic limestone drains (ALDs) rely on the use of crushed limestone to generate alkalinity and raise solution pH, allowing effective precipitation of metal hydroxides. However, a number of studies have demonstrated that calcite also has a small sorption capacity for divalent metal cations, especially Zn (Zachara et al., 1991; Uygur and Rimmer, 2000). Metal removal by calcite is thought to occur initially by adsorption reactions, as divalent metal cations have been shown to associate with the surface of calcite at low concentrations (Zachara et al., 1991). As sorption sites become saturated, metal removal may continue by formation of metal-carbonate precipitates on the calcite surface. One of the first PRB systems installed in the UK used limestone as its primary component. The PRB was installed at the Shilbottle colliery in Northumberland in the summer of 2002 and was designed to treat ochreous, metal-rich, acidic (pH~4) waters draining from the site (Jarvis et al., 2006). The PRB was composed primarily of limestone (50% limestone, 25% green waste compost and 25% slurry screenings), and monitoring data to date have shown high rates of metal removal (in particular Fe, Al, Zn and Ni) and an increase in pH.

A number of factors have shown to affect water remediation using carbonate materials, including solution pH and the metal contaminants present. For example
adsorption studies by Zachara et al. (1991) found that the strength of metal sorption onto calcite was particularly dependent upon the ionic radius of the ion. Metals with an ionic radius smaller than Ca (i.e. Cd, Mn, Zn, Co and Ni) were found to be more strongly sorbed, whereas sorption was weaker for metals such as Ba and Sr with an ionic radius greater than that of Ca. The amount of metal sorption onto calcite has also shown to vary with solution pH, with increased amounts of sorption generally occurring at higher pH values (Zachara et al., 1991; Ettler et al., 2006) (Figure 1.5(b)). This is partially due to the increasingly negative charge of the calcite surface with an increase in pH, which promotes sorption of free metal cations in solution. It is also likely that the increased amounts of H\(^+\) in solution at lower pH compete with metal ions for sorption sites, therefore resulting in lower amounts of metal removal. For this reason, carbonate minerals may in fact be much more effectively used to remove metal contaminants from circum-neutral mine drainage waters compared to AMD waters.

1.7.3.4. Clay minerals

The adsorption of metal ions by clay minerals has been well-documented in the literature for several decades (Gonzales-Pradas et al., 1994; Kaya and Ören, 2005). The ability of clays to remove metals from contaminated waters is primarily a result of their high surface area and cation exchange capacity (CEC). The surfaces of clay minerals are commonly occupied by hydrated cations such as Ca\(^{2+}\), K\(^+\) and Na\(^+\), which can easily exchange for metal cations (e.g. Zn, Cu, Pb, Ni) in solution.

Bentonite, a smectite group clay mineral, has been found to be a particularly effective material for the removal of organic and inorganic contaminants from waste water streams (Kapoor and Viraraghavan, 1998; Alvarez-Ayuso and Garcia-Sanchez, 2003; Kaya and Ören, 2005). Bentonite is a 2:1 clay mineral consisting of 2 silica sheets and one octahedral sheet, often with unbalanced charges at the mineral surface. These charge deficiencies, combined with the weak forces which hold the sheets together means that water can easily penetrate into the bentonite structure and the charge deficiencies may be balanced by metal cations (Kaya and Ören, 2005). Although bentonites are generally characterised by low hydraulic conductivities (\(\leq 10^{-9}\) m s\(^{-1}\)), they are also valued for their sorptive properties. For example Naseem
and Tahir, (2001) demonstrated the ability of bentonites to rapidly remove Pb from solution.

Adsorption onto the clay surface has shown to be extremely rapid. For example Bourg and Filby (1976) demonstrated that uptake of Zn$^{2+}$ ions onto a montmorillonite surface was virtually complete after ~15 minutes. For this reason, clays may be extremely effective for metal removal from wastewater streams. In spite of their low permeability, there is the possibility that clays could be combined with more permeable materials to create an effective reactive mixture for use in a PRB.

Sorption of metals onto clays has been found to be strongly pH-dependent (e.g. Farrah and Pickering, 1979), with significant reduction in sorption occurring at acidic pH. This is primarily thought to relate to the loss of the crystalline structure in bentonite at low pH values, therefore minimising its sorption capacity. Additional reasons for this pH-dependent sorption include the dissolution of Al from the clay surfaces at pH values <4, with the free Al ions then competing with the contaminant metal ions for sorption sites (Itami and Yanai, 2006). The competition of H$^+$ ions for sorption sites at acidic pH values (<4) will also decrease the amount of metal ion removal by clays (Kaya and Ören, 2005). For this reason, clays may represent a potentially effective reactive media for the removal of metal ions from circum-neutral mine waters.

1.7.3.5. Organic materials

Organic materials are commonly used reactive media in PRBs, as they are known to promote SO$_4^{2-}$ reduction, thereby causing a net increase in pH and resulting in the precipitation as sulphides of metal cations such as Cu, Zn, Pb, Cd, Ni and Fe (Blowes et al., 1998; Striegel et al., 2001). Commonly used organic materials include compost (Gibert et al., 2005a,b), leaf mulch, peat (Ho and McKay, 2004) and sawdust. These materials have the advantage that they are relatively inexpensive and are often readily available as waste products. The relative efficiencies of the most-commonly used organic materials to treat metal mine drainage water are considered below.
(i) Compost

A number of passive treatment systems have successfully used compost to neutralise and remediate acid mine drainage waters. In these systems metal removal is aided by an increase in pH, causing metal sulphide and (oxy)hydroxide precipitation (Hedin et al., 1994; McGregor et al., 2002). However, a number of studies have also demonstrated that in low-Fe waters metal removal may also take place by sorption onto the compost surface. For example Gibert et al. (2005a) studied metal attenuation by a compost/limestone mixture and concluded that over 99% of Fe, Al and Cu and over 60% Zn could be removed by a combination of (i) precipitation of (oxy)hydroxides and hydrated carbonates (ii) co-precipitation with Fe- and Al-(oxy)hydroxides and (iii) sorption onto the compost surface. Sorption was found to be a particularly important mechanism for Zn removal, as Zn is not expected to precipitate as a hydroxide in the pH region of 6-7. Compost could represent a potentially low-cost sorbent for the removal of metal ions (especially Zn) from circum-neutral mine drainage waters as the metal loading of compost has been found to increase at higher pH values (Gibert et al., 2005b), indicating that greater levels of metal removal could be achieved at circum-neutral pH.

(ii) Peat

The ability of peat to adsorb and retain metal cations has been recognised for some time. In the early 1980s there were a number of published studies reporting elevated metal concentrations in many of the native peatlands of northern Europe, often to the extent that economic extraction of the metals was being considered. More recently, peat has been successfully used in a number of remediation schemes to remove contaminant metal ions from wastewater streams (Brown et al., 2000; Ho and McKay, 2004).

Peat is essentially a partially decomposed mass of vegetative matter, which forms under wet, anoxic conditions where the rate of plant material accumulation is greater than the rate of decomposition. Peats are typically spongy in nature, with a high surface area (>200m$^2$ g$^{-1}$), a high porosity and a high CEC (Asplund et al., 1972). The ability of peat to remove metal contaminants from wastewaters is thought to
relate to its high content of lignin and humic acid, which possess polar functional groups that are commonly involved in chemical bonding (alcohols, aldehydes, ketones, acids, and ethers). These polar characteristics of peat mean that it has a high affinity for metal ions, with certain estimates stating that peat can adsorb metals up to 4% of its dry weight (Coupal and Lalancette, 1976).

Peat has excellent ion-exchange properties and is a natural pH buffer (Ho and McKay, 2004), making it an effective material for the removal of metal ions from contaminated water streams, particularly from AMD systems. It is also widely available and relatively inexpensive. Metal removal is thought to occur by ion-exchange reactions, whereby metal contaminants displace either H⁺ ions (at low pH values) or existing metal ions (at higher pH values) from the peat structure (Crist et al., 1996; Scherer et al., 2000). Additional potential mechanisms for metal removal by peat include surface adsorption, chemisorption and surface complexation (Brown et al., 2000).

Sorption onto peat has been shown to occur very rapidly, with maximum adsorption occurring after approximately 20 minutes (Ong and Swanson, 1966). Once this reaction is complete, leaching or desorption of the metal ions from the peat structure has shown to be minimal, therefore ensuring that contaminants are retained on the peat and are not released back into the water stream. Again, this is a desirable characteristic in a potential reactive material for a PRB system.

The efficiency of peat to remove metal ions from contaminated waters has shown to be strongly dependent on the major ion content of the water, solution pH and the contaminant of interest. Adsorption of metals has shown to be most effective at slightly acidic to circum-neutral pH; at low pH values (<3) metals will be leached from the peat, whereas at pH values above 8.5 the peat itself has shown to be unstable. Therefore treatment is most effective when the solution pH is somewhere between these two values (Coupal and Lalancette, 1976; Crist et al., 1996). Enhanced sorption of Zn in particular has shown to occur at higher pH values (McKay and Allen, 1997). For this reason alone, peat could represent a potential candidate material for the remediation of circum-neutral mine waters, particularly those with high dissolved Zn concentrations.
1.7.3.6. Zeolites

The use of natural zeolites for the removal of metal cations from wastewater streams has been well documented due to their excellent ion-exchange properties. Zeolites are crystalline aluminosilicate minerals, composed primarily of SiO$_4$ and AlO$_4$ tetrahedra connected by shared oxygen atoms (Leionen and Lehto, 2001; Hui et al., 2005). The nature in which the atoms are arranged means that zeolites possess sites that are generally occupied by exchangeable ions (e.g. Ca, Mg, K), and which may substitute for metal cations within solution by the process of ion exchange. They are especially desirable as they are relatively inexpensive and release only benign elements (e.g. Ca, Na, Mg and K) as a result of the ion exchange that takes place during water treatment. For example studies of metal sorption onto zeolites by Hui et al. (2005) found that only Si$^{4+}$, Al$^{3+}$ and Na$^{+}$ ions were released into solution as a result of treatment.

The effectiveness of zeolites for the treatment of waters has shown to be dependent upon a number of factors, including solution pH, initial metal concentrations (Bish and Ming, 2001) and metal ions present. Treatment of waters with a low initial pH may not be as effective, as a result of competition for exchange sites by H$^+$ ions. Metal removal by zeolites typically increases with increasing pH ($\leq$ pH 8) (Hui et al., 2005). Above pH 8 the zeolite surface is positively-charged, which may result in repulsion of contaminant metal ions. Zeolites have shown to be strongly ion-selective, and have selectivity sequences generally of the order Pb>Cd>Cu>Zn>Ni (Fujimori and Moriya, 1973; Semmens and Seyfarth, 1978; Kalita and Chelishchev, 1995). This selectivity for ion exchange has also shown to be affected by the presence of major ions such as Ca, Mg, Na and K in solution (Bish and Ming, 2001). For this reason, treatment of Ca- and Mg-rich waters using zeolites may be less effective.

A number of recent studies have looked at the sorption of divalent metal cations onto both natural and synthetic zeolites, particularly Cu (Guangsheng et al., 1988), Pb, Cd and Zn from wastewater streams (Semmens and Martin, 1988 in Bish and Ming, 2001). Although natural zeolites are significantly less expensive than their synthetic
counterparts, several studies (e.g. Panayotova and Velikov, 2002) have demonstrated that their sorption capacity may be as much as 10 times less.

Zeolites are better suited to the treatment of circum-neutral mine waters than AMD, as they are stable only in the pH range of 4-9 (this is a result of the high solubility of Al at extremely low and high pH values). Zeolites also have the potential to treat a wide range of contaminants, as the size and shape of the pores can be highly variable.

1.7.3.7. Phosphates

To date, phosphates have most commonly been used to immobilise contaminants in soils and to stabilise mine waste tailings by preventing the oxidation of sulphide minerals (Cotter-Howells and Caporn, 1996; Chen et al., 1997; Hodson et al., 2001; Cao et al., 2004; Harris and Lottermoser, 2006). Phosphate application has particularly been used to immobilise Pb in contaminated soils, as the Pb phosphates (e.g. hydroxypyromorphite) that form are highly insoluble, therefore preventing further leaching of contaminants through the soil profile and minimising their uptake by plants. A number of forms of phosphate have been used to remediate Pb-, Zn-, and Cd-contaminated soils, including phosphate rock (PR) (Hettiarachchi et al., 2001; Cao et al., 2004), mineral apatite and calcium phosphate or bone meal (Hodson et al., 2001; Sneddon et al., 2006). These materials have all proved effective at immobilising contaminants in soils, however the application of phosphates for water remediation has been relatively limited to date, and much of the published work on the phosphate-remediation of waters has concentrated on the treatment of radionuclides (Bostick et al., 1999; Fuller et al., 2002) and chlorinated organic compounds (Conca et al., 2000).

Metal removal by phosphates is thought to occur through a variety of processes. In the case of an apatite PRB, dissolution of the mineral apatite is thought to release sufficient quantities of $\text{PO}_4^{3-}$ ions into solution to exceed the solubility products of metal phosphates, causing them to precipitate. This mechanism is thought to be the primary mechanism for Pb removal, with interaction of apatite with aqueous Pb resulting in the formation of insoluble pyromorphites (Chen et al., 1997). Mechanisms for Zn and Cd removal using apatites are not so well understood, but
are thought to include precipitation of otavite (CdCO$_3$), hopeite (Zn$_3$(PO$_4$)$_4$.4H$_2$O) and zincite (ZnO) (Chen et al., 1997). Metal sorption onto the mineral surface and exchange of metal ions with Na and Ca ions in the apatite structure are also thought to play some role in metal removal. The dissolution of apatite during treatment also buffers the solution pH to around neutral, and this alone is thought to be sufficient to cause precipitation of some metals.

A limited number of studies have looked at the use of phosphates to remove a number of metal contaminants from aqueous solutions, including Pb, Cd, Zn and Cu. For example Chen et al. (1997) studied Pb, Cd and Zn sorption from aqueous solutions onto mineral apatite (the primary mineral component in phosphate rock). The results demonstrated that apatite could be used to effectively reduce metal concentrations to below the US EPA maximum allowable levels, with removal of Pb being particularly effective. More recently, an Apatite II Permeable Reactive Barrier was installed at the Silver Valley Mining District of northern Idaho in 2001 to treat elevated levels Zn, Cd, Pb, Cu, SO$_4$ and NO$_3$ (Conca and Wright, 2006). Performance monitoring over the first four years of operation has shown that the barrier has effectively removed an estimated 4550 kg Zn, 91 kg Pb and 45 kg Cd, with levels of Cd and Pb in the effluent being consistently reduced to below detection limit (2 µg L$^{-1}$) and levels of Zn being reduced to near background levels (~100 µg L$^{-1}$). A number of additional studies have demonstrated that a range of natural apatite materials such as bone meal, phosphate rock and bone char apatites can also be used to successfully treat metal-contaminated mine drainage waters (Fuller et al., 2002; Cao et al., 2004), with metals being removed by the formation of poorly-soluble metal phosphate phases. These results combined with the low cost, low solubility and chemical stability of phosphates means that they represent a potentially suitable reactive material for the treatment of metal-laden, circum-neutral mine waters.

1.7.3.8. Waste materials

A number of recent studies have proved the efficiency of a range of industrial bi-products and waste materials for the treatment of contaminated waters. These materials offer cheaper alternatives than traditionally used reactive products such as
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activated carbon, and often have extremely high sorption capacities. For example a number of authors have demonstrated the efficiency of wood, chitin, coconut shell, clay soil, fly ash and calcified seaweed in removing Cu, Pb, Zn, Hg and Cd from contaminated waters produced by industry (Bailey et al., 1999; Wantanaphong et al., 2004).

(i) Fly Ash

Fly ash is a waste product that is produced in multiple-tonne quantities by coal and thermal power plants. It is composed primarily of carbon and also oxides of silica, alumina and iron and has been shown to have adsorption capabilities for Pb (Woolard et al., 2000), Cu (Hequet et al., 2001) and Zn (Gupta and Sharma, 2003). The high metal removal capacities of fly ash are related primarily to its high metallic oxide content and large surface area, which makes it highly reactive. Fly ash is generally very alkaline in nature and often has a high CaO content. As a result, addition of fly ash to water results in a solution pH between 10 and 13, which promotes the precipitation of metal hydroxides (Zoumis et al., 2000; Cho et al., 2005; Erol et al., 2005). This is thought to be the primary method of metal removal by fly ash, with sorption of metals onto the surface of the reactive material playing a much smaller role. Erol et al. (2005) also recognise the importance that the alkaline properties of fly ash play in its ability to remove metal ions from wastewaters. A number of laboratory-based experiments (Zoumis et al., 2000; Wantanaphong et al., 2004; Erol et al., 2005) have indicated that fly ash is highly effective at metal removal and may be particularly suitable for the remediation of circum-neutral mine waters. Indeed, many studies have demonstrated that metal removal by fly ashes is highly dependent on solution pH, with greater amounts of removal occurring at higher pH values. For example Panday et al. (1985) studied Cu removal by Turkish fly ashes and found that metal removal increased from 13.9% at pH 3.0 to 100% at pH 8.0. Cho et al. (2005) found particularly high levels of metal removal by fly ash at circum-neutral pH, even when a low dosage of fly ash was used. Metal removal by fly ash has been seen to occur very rapidly. For example Panday et al. (1985) found the process to be almost spontaneous, whilst Bayat (2002b) observed high levels of metal removal after contact periods of less than 30 minutes.
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The fact that fly ash is produced as a waste product and typically sent to landfill means that there are many readily-available sources of a potentially-viable reactive material that may be available at little or no cost. In the USA, for example, approximately 40 million tonnes of fly ash are disposed of on an annual basis, costing an estimated US $1.2 billion (Dermatas and Meng, 2003). The use of fly ash as a reactive material in remediation would therefore negate the need for their specialised disposal elsewhere, potentially offering capital savings. Although in reality the quantities of fly ash used in remediation schemes would be small in comparison to the amount of material produced each year.

1.7.4. Summary

Previous research (summarised in section 1.7.3.) has identified a number of reactive materials that are potentially suitable for the remediation of circum-neutral pH waters. These are generally materials where sorption may be the dominant metal removal mechanism, or materials which promote an increase in solution pH, therefore encouraging metal removal by hydroxide precipitation. These include ZVI, activated carbon, fly ash, compost, clays, zeolites and carbonate minerals. The ability of a selection of these materials to remove Zn, Pb and Cd from circum-neutral mine waters will be investigated further in laboratory batch and column experiments (Chapters 4 and 5).

1.8. Additional considerations in Permeable Reactive Barrier design

Reactive material selection is a critical step in the PRB design process, but there are a number of additional considerations when developing a full-scale PRB system, including barrier layout, permeability, residence times and flow rates.

At present, there are two main commercial PRB designs in use: (i) the funnel and gate system and (ii) the continuous wall design (US EPA, 1998). The installation of both systems generally involves the emplacement of the selected mixture of reactive materials in a trench at shallow depths (<21 metres), thereby replacing the native aquifer material (Freethey et al., 2002). The funnel and gate system essentially
channels the groundwater flow to the zone of reactive materials by installing impermeable sheet pilings to either side (Figure 1.7). This system is most effective for large or deep contaminant plumes and essentially prevents the contaminated groundwater from flowing around the PRB. Funnel and gate PRBs are especially suitable when reactive materials are scarce or expensive, as the impermeable pilings to either side of the barrier allow groundwater flow to be channelled through a much smaller zone of reactive material. As the majority of PRBs use inexpensive and readily available materials, however, a continuous wall design is the more common approach. The continuous wall PRB design consists of a wall of reactive materials that has been installed in a trench. This design allows water to flow through the barrier system under its own hydraulic gradient.

Barrier permeability plays an important role in PRB design, and this will depend upon both the reactive material chosen and the geology of the surrounding aquifer material. In order to ensure uniform flow through the barrier system, the barrier should ideally have a hydraulic conductivity that is equal to or greater than that of the surrounding aquifer (Blowes et al., 2003). Gavaskar et al. (1998) even suggest that the hydraulic conductivity of the PRB should be 10 times that of the surrounding
geology. In order to achieve this desired combination of reactivity and permeability within a PRB it may be necessary to use a mixture of reactive materials. Many field-scale PRB systems also use a pea-gravel layer both up and down gradient of the PRB in order to ensure uniform flow throughout the barrier system (e.g. Morrison et al., 2002; Naftz et al., 2002).

During the design of a PRB, the thickness of the reactive wall must also be calculated and this involves consideration of flow, rates, residence times and rates of contaminant removal within the barrier system. The residence time of the groundwater within the PRB system is an important concept, as it will determine the length of the contact time between the reactive material and the contaminated water. Residence times are primarily dependent upon the reaction rates between the contaminants and the reactive material. Initial estimates of reaction rates may be obtained using laboratory batch and column experiments. These data may then be used to calculate residence times within full-scale PRB systems. Residence times vary significantly depending on the reactive material and the contaminant of interest. Many organic compounds require a residence time of several hours, however many metals and radionuclides have been shown to be reduced to acceptable concentrations within several minutes (Morrison et al., 2002). As a result, the majority of reactive barrier systems are only a couple of metres in thickness. For example the ZVI PRB at Fry Canyon, Utah is 2.1m thick (Rowland, 2002), the municipal compost PRB at Nickel Rim, Ontario is 4.0m in thickness, whilst the ZVI PRB at Oak Ridge, Tennessee only requires a thickness of 0.6m in order to reduce contaminant concentrations to acceptable levels (Gu et al., 2002).

An essential part of the PRB design process is the placement of monitoring wells both up- and down-gradient of the PRB. Determination of influent and effluent water quality can therefore allow PRB performance be monitored. Long-term performance monitoring of reactive barrier systems is essential, as a number of studies have demonstrated that PRB permeability may be reduced over time, as a result of clogging with metal precipitates or biofilms (Scherer et al., 2000; Gu et al., 2002). For example Morrison et al. (2002) studied mineral precipitation in a ZVI PRB and found that calcite precipitation was occurring at a rate of 50kg day$^{-1}$, representing almost a 10% loss in permeability. Reactivity is also likely to be affected by mineral
precipitation and monitoring is therefore vital to ensure that barrier performance does not decline significantly over time.

1.9. Effects of water hydrochemistry and pH on treatment efficiency

Batty and Younger (2004) recognise the importance of mine hydrochemistry to treatment efficiency, stating that ‘each mine displays a unique combination of pH, conductivity and relative abundances of different metal ions, which makes the treatment of such waters difficult’. The majority of the literature on metal sorption agrees that solution pH plays an important role in the ability of reactive materials to adsorb and retain metal ions (e.g. Farrah and Pickering, 1979; Stahl and James, 1991; Willow and Cohen, 2003). Solution pH affects not only the nature of the reactive material surface, but also metal speciation, precipitation and sorption. The majority of the literature is in agreement that metal removal is enhanced at higher pH values, due to reduced competitive sorption effects and deprotonation of the reactive material surface. This therefore represents an encouraging result for the successful remediation of metal-laden, circum-neutral mine waters.

In general, metal sorption is greater at higher pH values and this can be attributed to a number of factors. Much of the pH effect on metal sorption is a result of the competitive sorption of cations, with H$^+$ ions being preferentially adsorbed at low pH values. However, at neutral to alkaline pH values the activity of H$^+$ ions in solution is reduced, therefore favouring adsorption of metal cations by mass action (Lee and Saunders, 2003). e.g. sorption of metal cations can be considered as follows:

$$\text{FeOH} + \text{Zn}^{2+} \rightarrow \text{FeOZn}^+ + \text{H}^+$$  \[1.11\]

At neutral pH values, the concentration of H$^+$ ions (equation [1.11]) will be decreased, therefore driving this reaction towards the right and favouring the sorption of Zn. This pH-effect is the same for other metal cations.

Metal removal is dependent not only on solution pH, but also on the metal ions involved and the nature of the adsorbing surface. For example Barrow and Whelan
(1998) studied metal sorption by goethite and found that the effects of pH on sorption were much greater for Zn than for Cd, Co and Ni. The variations in solution pH also determine the surface charge of the reactive materials, with anion sorption (e.g. MoO$_4^{2-}$, CrO$_4^{2-}$) generally being favoured at low pH as a result of the net-positive charge on the surface of the reactive material. However, deprotonation of the reactive material as the solution pH increases means that cation sorption is increasingly favoured (e.g. Cd$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Pb$^{2+}$) (Scherer et al., 2000). As a result, metal cation removal is generally more effective at higher, circum-neutral pH values.

Solution pH has been shown to affect the amount of metal removal by a number of reactive materials. For example Chen et al. (1997) studied metal sorption from single- and multi-metal systems onto mineral apatite and found that removal of Zn and Cd by apatite was found to increase with increasing pH. Similarly, Dzombak and Morel (1990) studied metal sorption onto hydrous ferric hydroxides, and found that sorption of Zn, Cd, Co and Ni only take place at neutral to alkaline pH conditions. This is thought to be a result of deprotonation of the reactive material surface as the pH increases; at low pH values the surface of the sorbent holds mainly protonated sites and therefore has a net positive charge (Lee and Saunders, 2003). As the pH increases, this positive charge decreases, thus increasing the electrical attraction between the positively-charged metal cations in solution and the sorbent, effectively resulting in greater amounts of sorption. Studies on the pH effect of metal sorption by clays indicate that the competitive effect of protons for sorption sites should cease by $\sim$pH$>6$, and metal concentrations on the reactive material surface should be approaching maximum levels at around this pH value (Farrah and Pickering, 1979).

The majority of biosorbents for metal ions are also most effective in the pH range of 4-7, with optimum sorption capacities occurring at higher pH values (Edyvean et al., 1997). Bencheikh-Lehocine (1989) noted that Zn removal in particular is considerably enhanced at higher pH values. For these reasons, removal of metals from low Fe, circum-neutral mine drainage waters may prove to be less challenging than previously considered. Although metal removal rates by co-precipitation with Fe above the pH of Fe hydrolysis will be minimal, the increased amounts of metal sorption occurring at circum-neutral to alkaline pH values could result in significant amounts of metal removal by adsorptive processes.
1.9.1. Competitive sorption effects

Metal removal by reactive materials is affected not only by the major ion content of the groundwater, but also by the presence of other contaminant metal ions. For example metal removal may be adversely affected in systems contaminated by a number of metal ions, due to competition for sorption sites. Adsorption efficiency in multi-ion systems has generally found to be approximately of the order Pb$^{2+}$ > Cu$^{2+}$, Cd$^{2+}$ > Zn$^{2+}$ > Ca$^{2+}$ (Bunzl et al., 1976). For this reason, remediation of multi-metal contaminant streams may require the use of a mixture of reactive materials in order to provide effective treatment.

1.9.2. Effects of major ion chemistry on metal removal

The major ion chemistry of the solution has been shown to play an important role in treatment efficiency. A number of recent studies have looked at the extent to which major ion chemistry affects metal ion adsorption onto reactive materials. For example major ions such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$, Cl$^-$, CO$_3^{2-}$ and SO$_4^{2-}$ are known to bind to the reactive material surface and compete for adsorption sites with contaminant metal cations that are present in much lower concentrations. For example Mg$^{2+}$ (ionic radius = 0.080 nm) has the same valency and a similar atomic radius to Zn$^{2+}$ (ionic radius = 0.083 nm), and it would therefore be expected that the presence of high concentrations of Mg in solution would drastically reduce the amount of Zn sorption. A study by Ankomah (1992) looked at the effect of Mg and solution pH on Zn sorption by goethite. The results showed that at pH values < 7 the presence of Mg in solution was found to reduce the amount of Zn sorption occurring. However, at pH 7.8 and 8.5, Mg was seen to have practically no effect on Zn sorption by goethite. It is therefore likely that the competitive sorption of ions is not simply related to the ionic radius and the charge of the ion, but also its hydrolytic properties (pK values) and the solution pH.

The presence of carbonate species in solution is an additional parameter that has been shown to affect metal removal (Van Geen et al., 1994; Duff and Amrhein, 1996; Schulthess et al., 1998). For example Scherer et al. (2000) demonstrated that the presence of CO$_3^{2-}$ in solution affected the amount of Pb removal by hydroxyapatites,
as a result of its lower solubility at high pH values. As many of the metal mines in the UK and Ireland with circum-neutral mine drainage are located in areas with carbonate bedrock, the drainage waters are likely to contain significant concentrations of Ca, Mg and bicarbonate ($\text{HCO}_3^-$) in solution. The competitive sorption effects of these major cations and their tendency to form mineral precipitates as demonstrated by other studies (Schulthess et al., 1998; Gu et al., 2002) may have a detrimental effect on the treatment of metal-laden, circum-neutral mine waters. However, it also possible that high concentrations of carbonate in solution may in fact aid remediation by precipitation of metals as metal carbonates (Aziz et al., 2008).

It is important to note that the relative effect of groundwater hydrochemistry on treatment efficiency is dependent upon the reactive material used. For example $\text{SO}_4^{2-}$, $\text{NO}_3^-$ and $\text{HCO}_3^-$ are all corrosive to ZVI (Agrawal et al., 1995), whilst additional groundwater parameters such as $\text{Ca}^{2+}$ concentrations and dissolved oxygen content are also known to affect ZVI performance (Gu et al., 2002). For this reason, it is essential to characterise the full hydrochemistry of the metal-rich waters in order to predict the behaviour of different permeable reactive materials. This can be effectively done in the laboratory using batch and column treatability studies prior to the installation of field-scale and full-scale barrier systems.