Introduction
Arsenic can occur in several oxidation states in natural waters (-3, 0, +3 and +5) although the trivalent arsenite (As III) or pentavalent arsenate (As V) are the most common (Smedley and Kinnisburgh 2002). The most thermodynamically stable species over the natural range of soil pH of 4—7 is As(OH)₃ and in acid mine drainage waters (pH 2 – 5) H₂AsO₄⁻. The kinetics of As redox reactions is not rapid, so the predicted proportions of As species based on thermodynamic calculations do not always correspond to analytical results (O’Neil, 1990). An Eh-pH diagram showing the thermodynamically stable regions for arsenic species is shown in Figure 1. Dark grey areas on the plot correspond to aqueous species whilst light grey areas correspond to solid species.

Due to arsenic toxicity, the World Health Organisation as well as the USEPA has placed a guideline maximum allowable concentration of arsenic in drinking water of 10 µg/L (WHO, 1998). As (III) is considered to be more toxic than As (V); inorganic As (III) is a known and recognised human carcinogen with a poorly understood mechanism. When present, skin lesions are often in groups. In addition, there is a link between arsenic exposure and internal cancers of the bladder, liver, lungs and kidneys (Bhattacharyya et al., 2003). Initial symptoms of arsenic exposure are the formation of hyperpigmentation on the skin which usually appears as fine freckles distributed symmetrically and keratosis (formation of calluses).

Global Distribution of Arsenic
Arsenic is found to be truly globally distributed (Ravenscroft et al., 2001). There are a number of methods for mobilisation of arsenic into water which occur to varying degrees in different locations. These methods include: reductive dissolution of iron oxides releasing sorbed arsenic, oxidative dissolution of arsenic bearing pyrite, water-rock reaction with arsenic-bearing minerals, recrystallisation of reactive iron oxides into more stable phases, evaporative concentration of arsenic and competition by ion exchange of sorbed arsenic by other ions such as phosphate and bicarbonate.

Abstract
Arsenic impacts to natural and process waters have become an increasingly global problem with no economic boundaries, being prominent in many countries including Bangladesh, India, Pakistan, Mexico, Argentina, China, Ghana, USA and Canada and Europe (e.g. South West England). According to the WHO, arsenic is considered to be “of significant concern in several geographic areas”. Despite this there are limited proven industrial methods for efficient, low cost removal. In areas like Bangladesh where arsenic in groundwater is coupled with endemic poverty, a major problem lies in sourcing low cost solutions with minimal requirements for technical maintenance. In contrast, with high throughput applications for treating process waters to legal discharge limits at industrial operations, problems arise from production of hazardous solid or liquid wastes requiring disposal. Although innovative research continues to investigate these problems, peer reviewed publications focusing on demonstration or pilot plants remain elusive. The present review consolidates information on full scale and pilot plant operations for arsenic treatment. The lessons learned at these operations are applied to current novel research ideas. Recommendations are made for the most promising treatment options from an engineering standpoint in order to generate practical solutions for low cost and low discharge arsenic treatment.

Key Words arsenic, engineering, water treatment, pilot plant
A significant contribution to the release of arsenic to water supplies is the past or current activities in the mining industry (Welch, 2000). Oxidation of arsenic bearing sulfides (most importantly arsenopyrite) exposed by earth movement and water table depletion is the largest contributing factor to arsenic mobilisation at mine sites. Table 1 shows a summary of some well known arsenic occurrences worldwide with a brief description of the cause of mobility.

**Arsenic removal technology**

There are a number of different technologies for the removal of arsenic from natural waters which can subdivided as: chemical precipitation, adsorption, membrane filtration, in-situ treatment and biological remediation (see Table A-1 in supporting documents for examples of these technologies including advantages and disadvantages). Chemical precipitation, coagulation and filtration is the standard method for treating arsenic bearing waters industrially (Bowell, 2003). These plants require the use of a reagent to precipitate out arsenic flocs which are then removed by filtration. This method produces toxic sludge that requires disposal and very efficient pre-oxidation of arsenic present (Malik et al., 2009) which makes it undesirable from an efficiency and environmentally acceptable standpoint. New technologies are being researched which aim to create low cost treatment methods which minimise waste production and reagent use. Not all these innovative solutions are suitable for commercialisation and so current lab scale techniques need to be viewed in this light.

**Review of recent pilot plants**

The results of pilot plants and information regarding the operations of full scale commercial treatment plants are rarely submitted for publication in a peer reviewed journal. A major publisher of data on treatment plants is the USEPA (Lipps et al., 2010; Wang et al., 2011; Fields et al., 2000; Wang et al., 2000; Wilkin 2008). The lessons learned are important for considering and reviewing current lab scale research plans. To this end, reviews of different types of treatment plant are detailed below.

**Chemical Precipitation**

Although chemical oxidation and precipitation is the preferred treatment technology for arsenic bearing waters at present, it is not necessarily the most efficient or environmentally friendly. As such, this review aims to focus on the alternative technologies available. However, as most plants which currently treat mine water across the globe use this technology, no arsenic review would be complete without referring to it. Bowell (2003) presented this technology in terms of treatment plants under development at the time and stressed the importance of As (III) oxidation when using this technology. Different options for achieving this were presented, including a passive UV oxidation cell.

**Table 1** Summary of commonly cited examples of arsenic contamination in natural waters

<table>
<thead>
<tr>
<th>Region</th>
<th>Cause of arsenic mobilisation</th>
<th>Relevant Notes</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>South West USA</td>
<td>Iron oxide desorption due to changes in pH</td>
<td>Both mining related due to dewatering regimes and also due to natural processes</td>
<td>Welch et al., 2000</td>
</tr>
<tr>
<td>Eastern Croatia</td>
<td>Combination of desorption from iron oxides and desorption due to competition with bicarbonate anions</td>
<td>Concentrations up to 500 μg/L detected</td>
<td>Ujević et al., 2010</td>
</tr>
<tr>
<td>Northern China (Yuncheng Basin)</td>
<td>Inflows of sodium rich waters causing arsenic desorption from iron oxides</td>
<td>Competition with bicarbonate ions further increased arsenic desorption</td>
<td>Curell et al., 2011</td>
</tr>
<tr>
<td>Bangladesh</td>
<td>Reductive dissolution of iron oxides by anaerobic bacteria</td>
<td>Well known example of widespread arsenic contamination affecting 41 million people in Bangladesh and West Bengal</td>
<td>Ravenscroft et al., 2005; Nickson et al., 2000</td>
</tr>
<tr>
<td>Ashanti Mine, Ghana</td>
<td>Oxidation of arsenian pyrite as a result of mining</td>
<td>Localised effects due to mining conditions but high levels of arsenic up to 600 μg/L in pore water and 1300 ppm in soils</td>
<td>Bowell, 1994</td>
</tr>
<tr>
<td>San Juan Province, Argentina</td>
<td>Regional source of arsenic via evaporites with no concluded mobilisation mechanism</td>
<td>Concentrations in Rio Blanco up to 140 μg/L</td>
<td>Rawlins et al., 1997</td>
</tr>
<tr>
<td>Yellowknife, Canada</td>
<td>Mine water discharge due to association of gold ore with arsenopyrite</td>
<td>Lakes near Yellowknife with concentrations up to 5500 μg/L</td>
<td>Wagemann et al., 1978</td>
</tr>
</tbody>
</table>
Bowen Collins & Associates (2004) ran a coagulation/filtration plant in Mesquite, Nevada. This plant was chosen due to lower costs above a flow rate of 230 L/hour for the commercial plant. It was found that at the desired flow rate through the filter an iron dose of 2 mg/L was acceptable for a reduction of arsenic from 38 to <10 µg/L. An iron dose of 6 mg/L was required to reduce arsenic concentration to 5 µg/L. Increased iron doses and higher filtration rates had a linear effect to decrease filter life-time before backwashing was required. However, increased filtration rate appeared to have little effect on effluent arsenic concentration at high iron doses. The most important design parameter raised in the pilot study was that of the filter media. This design parameter must be suited to the precipitate formed as well as the required filtration rate.

**Adsorption**

Lipps et al. (2010) published a study for the USEPA on the use of adsorption columns to treat contaminated well water to the WHO guideline of 10 µg/L. The feed well water to the plant contained 34.6 to 50.2 µg/L of As, predominantly as As (III). Therefore an oxidative media was used in an initial column followed by absorptive media in three additional columns. The performance of the plant was assessed over a 2.5 year period. Over this time minimal engineering difficulties were encountered due to a very simple plant design that worked on passive principals. The only electronic systems were the well pump and a booster pump to send water to a pressure tank feeding the columns. After installation and commissioning there was no requirement for skilled operators to maintain the plant, apart from media replacement and monthly sediment filter inspections. Capital costs for a 3 m³/hour capacity plant was $16,457, 65% of which was for equipment. A quarter of the cost was for labour and installation which can be minimised. The major design parameter was absorptive media where breakthrough for one media was observed after only 6,300 bed volumes and for the other media 15,300 bed volumes. Optimisation of the media types lowered operational costs from $45,382/year to $2,849/year. Electrical pumping costs were negligible.

**Membrane Filtration**

Jessica et al. (2006) evaluated cost effectiveness of different arsenic avoidance techniques in the USA. Reverse Osmosis (RO) was found to be the most cost effective solution ($411/year) followed by activated alumina ($518/year). Wang et al. (2011) have recently released a report for the USEPA on a 10 month pilot scale point-of-entry RO treatment plant at an elementary school coupled with dual plumbing so that only potable water required treatment. The feed to the RO unit contained 18.2 µg/L of As, predominantly as As (V) and required filtering at 5 µm prior to treating. The performance of the plant was assessed over a 10 month period. During this time the RO feed pump required replacement, indicating the technical nature of this treatment option. After installation and commissioning there was no requirement for skilled operators to maintain the plant, apart from the pump replacement. Capital costs for a 0.2 m³/hour capacity plant was $20,542, although $8,600 was required for installation of a dual distribution system. The majority of operating cost was for operator inspection at 10 minutes a day ($666/year). However, this cost would remain fixed at higher throughputs. Electrical costs equated to 0.91 $/m³. Finally, it should be noted that the permeate was only 40% of the feed, so that 60% of the feed water was sent to septic discharge with a concentration of arsenic of approximately 32 µg/L. This treatment option is expensive for such a low flow rate plant and the efficiency is undesirable.

**In-Situ Treatment**

A field trial for enhanced natural attenuation was completed in Carson Valley, USA, with high alkalinity and low iron groundwater (Welch et al., 2008). The low iron meant there were minimal sites for arsenic adsorption and high pH acted to limit adsorption. Inorganic arsenic in the aquifer tested was in the range of 30 – 36 µg/L and was found in different oxidation states depending on the well sampled. Injection cycles of dissolved oxygen, iron II and hydrochloric acid were used to lower the pH and promote iron oxide formation in the aquifer. From aquifers containing As (V) the extracted waters had arsenic concentrations below the NDEP reference guideline although in some instances they exceeded the iron and manganese guideline concentration for the USEPA. This site would require intensive monitoring to strike a balance between arsenic removal and reagent addition to the aquifer. Unfortunately reagent consumption figures were not included in the paper.

In 2005 a permeable reactive barrier (PRB) of zero valent iron (ZVI) was installed at an old smelting site in Montana (Wilkin et al., 2008). This solution has successfully treated a point source of arsenic contamination in groundwater from an up-gradient concentration of over 25,000 µg/L to <10 µg/L within the barrier itself. The PRB had been operating successfully for 2 years. The major problem is that below the depth of the barrier there is still arsenic contamination in groundwater that is not attenuated. Unfortunately cost estimations were not included in the report.
The major recommendation of the project was that very thorough site characterisation is required prior to implementation, including detailed hydrogeological and hydrogeochemical understanding to produce models of arsenic load flows and permeability in the aquifer.

**Biological Remediation**

Bacteria can be used to enhance the rate of arsenic III oxidation by coupling the reaction to the reduction of oxygen or nitrate for energy (Wang and Zhao, 2009). This process can be used in order to detoxify arsenic to the more benign As (V) or as a means of pre-treatment to allow more efficient arsenic removal. In Malgara, northern Greece, an industrial water treatment plant has begun using biooxidation as a pre-treatment method to oxidise arsenic, ammonium and manganese (Katsyianiannis et al., 2008). The feed concentration of arsenic is 20 µg/L (70% as As (III)) and iron concentrations are particularly low at 165 µg/L. Final arsenic concentrations sent to the consumer are below 10 µg/L. Initial plant operation showed that the level of iron sorption sites was insufficient for As removal. Therefore, in order to remove arsenic the biologically oxidised As (V) is coagulated onto hydrous ferric oxides via hydrolysis of FeClSO₄ which are subsequently removed by filtration.

Phytoremediation makes use of some plants natural propensity to accumulate arsenic to anomalous concentrations. These technologies can offer a potentially low cost alternative for remediation of low-level contamination. A pilot plant in New Mexico (Elless et al., 2005) successfully produced arsenic free water at a maximum flow rate of 1,900 L/day over a 3-month period where breakthrough was not observed. However, it was necessary to rotate the plants through nutrient solutions during treatment. Water loss was only about 5% by evapotranspiration. The major drawbacks of the technology are lack of knowledge regarding plant stress factors that hinder growth of a crop at a large scale and high As concentrations, the disposal of the arsenic bearing biomass and the large area required for high flow rates. In addition, residence time for this design solution can be in the region of 5.5 hours compared with 0.3 hours for ion exchange. The capital costs for a 25 m³/hour plant would be in the region of $120,000. The majority of this cost would be in the construction of a greenhouse. Operating costs are expected to be in the region of $15,400/year which makes this solution highly cost effective for low flow and low level contamination areas.

**Considerations for Emerging solutions**

Some promising methods of arsenic removal from natural waters are currently being tested at the lab scale. It is often difficult or impossible to infer real world performance based on lab data. As such these efforts should be viewed in terms of likely commercialisation to aid in selection of technologies for pilot and demonstration plants going forward. Two examples of such treatment options are: membrane distillation (membrane filtration technology) and biosorption (adsorption biotechnology).

Manna et al. (2009) set up a membrane distillation facility in Bangladesh where water vapour passes through a membrane, condenses on the other side impurity free. A solar powered membrane distillation system was tested in South-East Asia where a feed of 200 µg/L arsenic was treated to below arsenic detection limits. The rate of the distillation process was 85 kg/m²/hour with a feed concentration of 600 µg/L. This suggests that a large footprint may be required. The design of the system is affordable and simple but may not be suited to large flows. This installation may help overcome the shortcomings of the membrane plant discussed above as there is no requirement for a high pressure pump and in addition there would not be large energy costs incurred for pumping. Further, fouling is less of a problem in this system so very fine 5 µm pre-filters are not required. This solution would need to be able to produce much lower reject percentage than the pilot RO plant.

Biosorption is the active removal of arsenic from water or soils via uptake by bacteria. The process involves the direct adsorption of arsenic followed by co-precipitation by with iron or manganese (Wang and Zhao, 2009). The general problem with these processes is the rate at which they can occur. Genetically modified E. Coli produced cells which accumulated 5 times as much As (III) and 60 times as much As (V). These cells were able to 98% of arsenic present in a sample of contaminated water (50 µg/L arsenic) within 1 hour (Kostal et al., 2004). The application of this type of high rate, high capacity adsorbent in a highly reliable and simple adsorption column like that discussed previously would generate a highly efficient solution to the problem of arsenic treatment.

**Conclusions**

It is important to take into account difficulties experienced in engineering designs for historical water treatment facilities when developing future treatment methods at the lab and bench scale. Major factors which affect this are: level of automation, requirements for skilled operation, reliability of design and prospective project costs.

From the pilot plants reviewed above it is believed that adsorption columns are the preferred treatment option for small scale potable water treatment in the future due to minimal moving.
parts, minimal automation or skilled operation and the potential for low cost and high capacity adsorbents to make this technology highly cost effective.

Mine waters contaminated with arsenic are usually point sources and the effects are often localised but can be at high concentrations. For this type of arsenic contamination, in-situ treatments appear to be particularly promising for future development. This is due to the ability to efficiently handle point sources in groundwater and at the same time be able to treat a wider area of contamination without costly infrastructure associated with very large flows. What is more, these treatments do not produce toxic sludge or brines and avoid the costly disposal commonly associated with arsenic treatment.

References

Bowell R.J., 1994, Arsenic speciation in soil porewaters from the Ashanti Mine, Ghana, Applied Geochemistry, 9, 15 – 22
Fields K., Chen A., Wang L., 2000, Arsenic removal from drinking water by iron removal plants, Ohio, EPA/600/R-00/086
O’Neil P., 1995, Arsenic, Heavy Metals in Soils, 83 – 99, Blackie and Sons, Glasgow
Rawlins B.G., Brewster N., Figueiredo B., Borba R., 1997, Preliminary investigation of mining related arsenic contamination in the provinces of Mendoza and San Juan (Argentina) and Minas Gerais state (Brazil), British Geological Survey, WC/97/60
Wang L., Chen A., Fields K., 2000, Arsenic Removal from Drinking Water by Ion Exchange and Activated Alumina Plants, Ohio, EPA/600/R-00/086
Wang L., Lewis G.M., Chen A., 2000, Arsenic and antimony removal from drinking water by point-of-entry reverse osmosis coupled with dual plumbing distribution, Ohio, EPA/600/R-11/026

WHO, 1998, Guidelines for drinking water quality, addendum to volume 1: Recommendations