In-situ immobilization of arsenic in the subsurface using ferrous chloride

by

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Abstract

At a military site in Northern Germany, the aquifer is contaminated by high quantities of arsenic (As) from chemical warfare agents (CWA) and their degradation products. Arsenic concentrations up to 9 mg L^{-1} were found (Krüger et al. 2008). In regards to this high degree of contamination, an in-situ arsenic remediation strategy using bivalent ferrous chloride ($FeCl_2$) was evaluated. The field trial spanned almost two years, and a total of 2.3 kg of As was immobilized through the pilot plant. The objective of the present study was to design a reactive transport model for the arsenic immobilization field trial, which would provide a quantitative framework to evaluate As fate in the aquifer system and indicate the effectiveness of the remediation technology. The completed model couples physical and geochemical processes governing the fate of As at the site and is transferable to similar case studies that involve arsenic contamination.

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Contributions of Authors

Roemer, M., Krüger, T., Wallis, I., Holländer, H. M. (in preparation). Reactive transport modeling of an in-situ immobilization trial of organically and inorganically bound arsenic species in the subsurface. Hydrogeology Journal.

a. Roemer, M.: Developed and implemented the methodology for the reactive transport model and wrote the paper
b. Krüger, T.: Planned, conducted and evaluated the field experiment for an in-situ immobilization of arsenic at the military site in Northern Germany, produced and provided the data, contributed to the framework of the methodology for the numerical modeling
c. Wallis, I.: Contributed to the set-up of the geochemical model and the editing of the paper
d. Holländer, H. M.: Suggested and supervised the research and assisted with the editing of the paper

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α_l	L	longitudinal dispersivity
α_t	L	transversal dispersivity
α_v	L	vertical dispersivity
C	ML^{-1}	concentration
C_S	MT^{-1}	concentration source and sink
$D_{i,j}$	L^2T^{-1}	dispersion coefficient in i- and j-direction
D_m	L^2T^{-1}	molecular diffusion coefficient
D^*	L^2T^{-1}	effective diffusion coefficient
E_h	$ML^2T^{-3}I^{-1}$	redox potential
EC	$L^{-3}M^{-1}T^3I^2$	electric conductivity
h	L	hydraulic head
J^{adv}	$ML^{-2}T^{-1}$	advective mass flux
J_{dif}	$ML^{-2}T^{-1}$	diffusive mass flux
J_{disp}	$ML^{-2}T^{-1}$	dispersive mass flux
K	LT^{-1}	hydraulic conductivity
K_d	LM^{-3}	distribution coefficient
K_F	L^3M^{-1}	Freundlich coefficient
K_L	L^3M^{-1}	Langmuir coefficient
L_i	L	distance in i-direction
L_j	L	distance in j-direction
log_k	-	adsorption constant
n	-	porosity
n_e	-	effective porosity
pH	-	negative of the base-10 logarithm of the activity of hydronium ions
q	T^{-1}	sink and source
Q	MM^{-1}	maximum sorption capacity
q_i	T^{-1}	volumetric fluxes associated with the source and sink
R_k	$ML^{-3}T^{-1}$	chemical reaction rate
S	MM^{-1}	mass of the solute loading on the adsorbent
S_S	L^{-1}	specific Storage
t	T	time

v_e	LT^{-1}	effective flow velocity
v_i	LT^{-1}	seepage or linear pore water velocity
$\partial h/\partial x,y,z$	-	hydraulic gradient in x-, y- and z-direction
τ	-	tortuosity
κ	LM^{-3}	Henry coefficient

List of Abbreviations

AA	activated alumina
AAs	aromatic arsenicals
AC	activated carbon
ADE	advection-dispersion equation
As	arsenic
As_i	inorganic arsenic
As_org	organic arsenic
As_t	total arsenic
ASR	aquifer storage and recovery
CCB	constant concentration boundary
CPB	cement paste backfill
CWA	chemical warfare agent
EPA	US Environmental Protection Agency
FDM	finite difference method
FeAsS	arsenopyrite
$FeCl_2$	bivalent ferrous chloride
$Fe(OH)_3$	iron (III) hydroxide
FeS_2	arsenian pyrite
Fe(II)	ferrous iron
Fe(III)	ferric iron
HFO	hydrous ferric oxide
MAC	maximum acceptable concentration
NAPL	non-aqueous phase liquids
PDE	partial differential equation
PRB	permeable reactive barrier
RMSE	root mean squared error
S/S	solidification/stabilisation
SCM	surface-complexation model
WHO	World Health Organisation
WW	World War

ZVI	zero-valent iron
1D	one dimensional
2D	two dimensional
3D	three dimensional

1. Introduction

Groundwater pollution in the form of arsenic (As) is a serious threat to many people around the globe. The element arsenic is known to be toxic to humans, animals, and plants (Bergqvist and Greger 2014; Finnegan and Chen 2012). Widely distributed in the environment as a metalloid, arsenic has been ranked twentieth in abundance of elements in the earth’s crust (Bissen and Frimmel 2003a). Arsenic soil contamination can be a result of naturally occurring geochemical sources, as well as anthropogenic activities. These manmade origins of contamination are, according to Bergqvist and Greger (2014), due to industrial activities including wood impregnation, oil refining, gas and coal processing, and military activities. During World Wars (WW) I and II, the military specifically produced and tested arsenic in chemical warfare agents (CWA) because of its high toxicity. Henriksson et al. (1996) pointed out that CWA may be more toxic on a cellular level in regards to pure arsenic. Along with other substances, As was predominantly present in so-called blue-cross CWA, where the blue-cross, or ring, was used to mark high volatility and high irritation potential, as Martinetz (1993) explained. Leading CWA contained aromatic arsenicals (AAs), including Clark I (diphenylchloroarsine), Clark II (diphenylcyanoarsine), and Adamsite (10-chloro-5,10-dihydrophenarseine) (Baba et al. 2008; Henriksson et al. 1996). In the Federal Republic of Germany, it was believed that over 3,200 military sites had been contaminated by 1996 (Thieme 1996). In many cases, soil contamination was introduced between and after the wars through improper methods of disposal, such as the incineration or burial of remaining CWA. Baba et al. (2008) reported that multiple countries including Germany, Japan and China disposed of CWA by sea-dumping and earth-burial, after WWII.

This study focused on a military site in Northern Germany, where the present aquifer system was contaminated through the infiltration of high quantities of As from CWA and their degradation products. About one quarter of the German Army's entire warfare ammunition was produced at the military site during WWI by more than 6,000 people (Grube 2016). At the end of WWI, the military site was primarily used for ammunition storage, and it was decided to dump the remains into the North Sea and the Baltic Sea. During the preparations, a train wagon loaded with warfare agents exploded at the site, causing severe damage to the surrounding facilities. The cleanup was poorly handled (Grube 2016). Remaining explosives were simply detonated on-site, resulting in widespread contamination in the local area. After WWII, remaining CWA at the site were burned together with kerosene as an accelerant in open zinc tanks. These tanks corroded over time and caused further contamination.

A field test was conducted in 2005 intended to determine the rate of As contamination at the military site in Northern Germany. The results showed total As concentrations (As_t) in the groundwater up to 9 mg L^{-1} (Holländer et al. 2008). The measured As was predominantly organically bound (As_org) and occurred in the form of phenylized As compounds. Inorganic As compounds (As_i: As^{3+} and As^{5+}) were additionally determined with an uptake of less than ten percent of the As_t in the aquifer system. In response to the high degree of contamination and the existing threat to surrounding groundwater pumping wells, a pilot plant was installed downstream from one of the hot spots for an in-situ immobilization of the remaining As_org and As_i compounds from former CWA. An upfront laboratory test (Holländer et al. 2008; Krüger et al. 2008) concluded that bivalent ferrous chloride ($FeCl_2$) would be best suited for the immobilization of various organic and inorganic As species. The field study spanned almost two years, during which a total of 2.3 kg of arsenic were immobilized through the pilot plant. The initial arsenic concentration in the vicinity of the pilot plant was reduced from 1.65 mg L^{-1} to less than 0.3 mg L^{-1} (Krüger et al. 2014). Collected groundwater samples showed remaining As_i-concentrations of less than one percent and As_org-concentrations of eighteen percent.

Numerical modeling was performed subsequently to the field experiment to simulate the remediation impact during the pilot study (Krüger et al. 2012). In order to represent the arsenic fate in the aquifer system, a numerical groundwater flow and solute transport model was coupled with a geochemical model. For the geochemical model configuration, the organically-bound and inorganic arsenic species were both considered as one hypothetical species to simplify the modeling process. However, in order to have a sufficient numerical model, both arsenic species needed to be implemented to adequately represent the arsenic fate. The provision of a proper geochemical model is crucial for the accurate projection of the technology for other scenarios and its transferability to other study sites.

1.1 Research Objective and Scope

The objective of the present study was to design a numerical flow and transport model for the arsenic immobilization field experiment conducted at the military site in Northern Germany, which provided a quantitative framework to evaluate the arsenic fate in the aquifer system. Both inorganic and organically-bound As were included as separate species into a geochemical model to most accurately represent the arsenic fate throughout the field experiment. To determine whether the model simulated reliable results it had to be calibrated and validated. This allowed for the use of the geochemical model for similar case studies that involve arsenic contamination. The numerical model offers an estimation of the remediation potential that could be achieved at each specified location. Finally, it can be used as a tool to determine the advantages of the new in-situ immobilization technique over other conservative treatment processes.

1.2 Thesis Organization

The present thesis is comprised of an extensive literature review (Chapter 2), that covers the main characteristics of arsenic occurrence and mobility in the groundwater. Secondly, different remediation technologies for arsenic removal from soil, waste and water are discussed and known case studies are revised. Thirdly, the in-situ immobilization of arsenic by metal salts is expanded upon in detail because it is a significant part of this research. Fourthly, a literature review for the remobilization of arsenic is provided. Finally, the modeling procedure for arsenic mobility is reviewed.

The second part of this thesis (Chapter 3) comprises a paper about the numerical modeling of the in-situ immobilization of arsenic for the field experiment conducted at the military site in Northern Germany. The methodology for the development of the reactive transport model is explained. The results from the numerical study are presented along with a discussion that shines further light on its performance and reliability. Finally, Chapters 4 and 5 summarize the research process and recommendations for future research are given.

2. Literature Review

The literature review section provides an overview of arsenic characteristics and its occurrence and behaviour in the subsurface. The following is a review of pre-existing arsenic remediation technologies and where they have been deployed. Moreover, the in-situ immobilization of arsenic by metal salts is described, which is based on the processes adsorption and precipitation explained in chapter 2.2.3 and was further expanded upon. The potential remobilization of the arsenic is then discussed, and the chapter concludes with an attempt to describe the numerical modeling of arsenic mobility as it stands today.

2.1 Arsenic Occurrence and Mobility

Arsenic occurs naturally in the environment and is found in volcanic rock, volcanic glass, aluminosilicate minerals, and igneous rocks. It may be adsorbed or co-precipitated with metal oxides or clay-mineral surfaces, or associated with sulfide minerals, pyrite, or organic matter (Welch et al. 1988). Additionally, arsenic may be of anthropogenic origin, being introduced to the environment through military or industrial activities, wood impregnation, oil refining, gas and coal processing, and ammunition and pesticide production (Bergqvist and Greger 2014). Arsenic contamination is a global problem. Countries such as India, Bangladesh and Argentina are particularly affected by elevated arsenic concentrations in the groundwater (Bissen and Frimmel 2003a; Das et al. 1996; Mandal and Suzuki 2002; Meng et al. 2001), but other countries including Canada contend with arsenic contamination (Martinez et al. 2013; McGuigan et al. 2010; Wang and Mulligan 2006). According to Wang and Mulligan (2006) As is introduced naturally in Canada as As-rich rocks weather and erode. However, As contamination in Canada has also become a result of current and former mining activities, especially in regards to gold processing, pesticides and wood preservatives and industrial and domestic activities.

A comprehensive review on As levels in Canadian drinking water has been presented by McGuigan et al. (2010), showing that in general the As level in municipal drinking water for

Canadian provinces is below the country's maximum acceptable concentration (MAC) and the World Health Organization (WHO) standard for As of 10 µg L^{-1} (Health Canada 2006; WHO 2011). Nevertheless, several provinces including Alberta, British Columbia, Manitoba, New Brunswick, Newfoundland and Labrador, Nova Scotia, Québec and Saskatchewan reported hotspots where As concentrations >10 mg L^{-1} occurred (McGuigan et al. 2010).

Arsenic occurrence in Canadian soil has been thoroughly reported by Wang and Mulligan (2006). They determined that arsenic concentrations in Canadian soil were primarily the result of natural occurrence or related to mining activities. Arsenic concentrations ranged between 4.8 – 13.6 mg kg^{-1} for uncontaminated soil (Health Canada 2006), but could be as high as 5,760 mg kg^{-1} for outcrop soil, sampled at the Giant Mine Site, Northwest Territories (Bromstad et al. 2017).

Not only is As found in Canadian soil and water, it is also present in the air. The arsenic concentration in the air has been studied from 1985 to 1990 in 11 Canadian cities and one rural area. Air measurements indicated arsenic levels in the range of <0.0005 to 0.017 µg m^{-3} based on a 24-hour average (Health Canada 2006). Nevertheless, As found in the Canadian atmosphere can be much higher due to anthropogenic sources including smelting, fossil-fuel combustion or other industrial activities (Wang and Mulligan 2006). ENVIRDOQ (1997), for example, reported a 24-h maximum As-concentration of 6.5 µg m^{-3} that was measured in the air near Rouyn-Noranda, a mining rich area in Québec. Federal guidelines as well as provincial and territorial standards are in place for arsenic contaminated sites and their remediation necessity (AEP 2016; Health Canada 2017). Arsenic contaminated sites in Canada and their treatment options have been discussed in the following chapters 2.2.1 to 2.2.4.

In terms of arsenic occurrence, inorganic arsenic is generally the main form of arsenic in the subsurface and most commonly occurs in the groundwater as the compounds arsenite (As^{+3}) and arsenate (As^{+5}). Arsenite predominantly occurs in reducing conditions as the compounds H_3AsO_3 or H_2AsO_3 at a pH of around 9 – 11, whereas arsenate is the predominant species in oxygenated water in the form of the compounds H_2AsO_4 and $HAsO_4$ at a pH between 4 to 10 (Barringer and Reilly 2013). Arsenic undergoes a range of different chemical reactions in the subsurface. Its speciation in the aqueous phase is controlled by the given pH, the redox potential (Eh), and biological activities. Figure 1 (Ferguson and Gavis 1972) describes the relationship between the redox potential and the pH in terms of their control of the arsenate/arsenite transition. Organic arsenic species are generally less abundant in the subsurface compared to inorganically bound arsenic species. Biomethylation and anthropogenic activities, such as agricultural practices and military activities, are known sources of organic As spreading in the subsurface (Baba et al. 2008; Huang et al. 2011; Köhler et al. 2001). Huang et al. (2011) explain that (pentavalent) organic arsenic is usually less toxic compared to arsenate and arsenite species. However, trivalent organic arsenic was found to have a higher toxicity than inorganic arsenic.

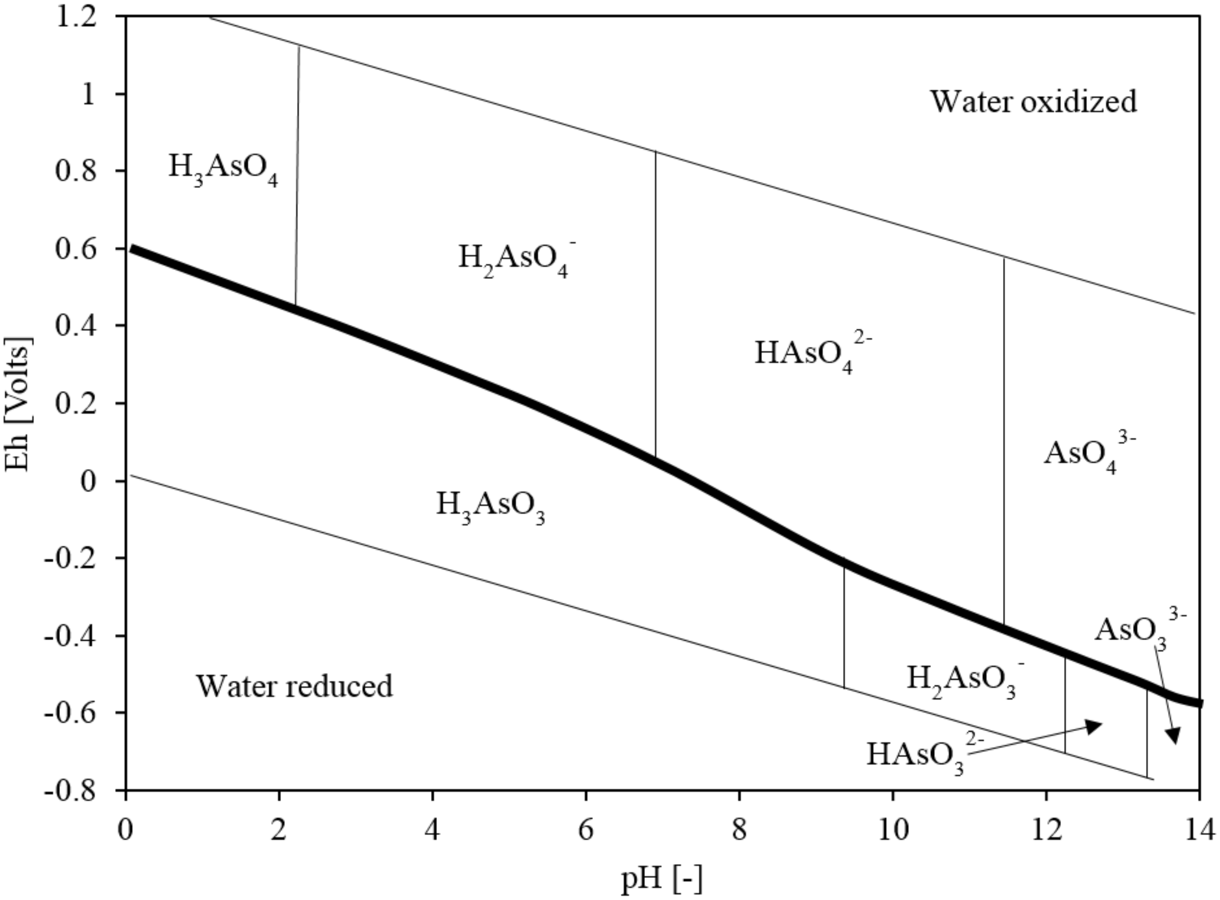

Fig. 1 Eh and pH control on arsenic speciation, modified from (Ferguson and Gavis 1972)

Major processes that control arsenic mobility in natural groundwater systems include adsorption and desorption, and solid-phase precipitation and dissolution (Hinkle and Polette 1999). For example, both arsenate and arsenite adsorb to the surface of minerals, such as ferric oxides or clay particles. These minerals are often present in sediments where naturally occurring arsenic exists. The surface characterization of present minerals is, therefore, an important indicator for the overall mobility of the arsenic. Conversely, reducing conditions in the aquifer system can lead to the destabilization of previously existing bonds, thus mobilizing the arsenic back into the aqueous phase. Desorption of arsenic from the adsorbent may occur under aerobic conditions for waters with pH-values that are greater than 8.0 and in the presence of nitrate or sulfate (Ravenscroft et al. 2009). Another mechanism that leads to the release of arsenic from geological material and ultimately a mobilization involves the dissolution-oxidation of arsenic bearing sulfides (Lengke et al. 2009). These sulfides include arsenopyrite (FeAsS) and arsenian pyrite (FeS_2). Aerobic conditions in the groundwater lead to the dissolution-oxidation of the arsenopyrite and the release of arsenic.

2.2 Arsenic Remediation Technologies

In the modern day, a variety of remediation methods exists for the treatment of arsenic-contaminated sites. These include in-situ and ex-situ methods, which are subdivided by the US Environmental Protection Agency EPA (2002) into Soil and Waste Treatment Technologies, Water Treatment Technologies, and Innovative Technologies. Conventional treatment processes such as coagulation with either alum or iron salts and subsequent filtration are commonly used by large-scale treatment facilities for the removal of arsenic from contaminated groundwater (Mulligan et al. 2005). Smaller municipalities more often use ion exchange adsorption in small-scale treatment systems for convenient handling of arsenic contaminated water (Clifford 1999). The provision of strict maximum arsenic concentrations in accordance with the WHO standard of 10 $\mu g\ L^{-1}$ in drinking water (WHO 2011) has led to the research and development of innovative technologies in recent years. Selecting or designing the proper technology depends on many different factors, such as the site-specific physical, chemical and biological characteristics, the degree of contamination, the expected remediation results/site specific target levels, the time required to achieve the necessary levels, the long-term reliability or feasibility of the technology, and the available budget for the remediation plan. Wang and Mulligan (2006) pointed out that in-situ remediation techniques are likely less expensive than ex-situ techniques in cases where the remediation is for large contaminated sites. Furthermore, ex-situ technologies tend to be more disruptive to the ecosystem and the local landscape. Litter et al. (2014) reported the development and advantages of new in-situ technologies for arsenic contaminated groundwater over conventional technologies.

A number of existing technologies are described in subchapters 2.2.1 to 2.2.4, following amongst other references the EPA (2002) report on Arsenic Treatment Technologies for Soil, Waste, and Water.

2.2.1 Traditional Treatment Methods

Excavation

The ex-situ remediation technique of excavation is a mechanical process that involves the physical removal of contaminated material and its transportation to regulated landfills (Meuser 2010). In cases where it is more efficient, the excavated soil may also be treated on-site in combination with additional treatment processes and followed by the reuse of the remediated soil as backfill material. Excavation is often used in cases where the contaminated soil is shallow and easy to access. This remediation method can be executed in a short amount of time while ensuring permanent removal of excavated pollutants. However, excavation often covers only a portion of the contaminant plume in the groundwater and is better suited for the treatment of contaminated soil than groundwater. Additional dewatering should be considered in cases where the groundwater makes contact with the contaminated soil (Meuser 2010). Excavation sufficiency is also dependent on the site-specific conditions because bedrock or pre-existing structures and roads can limit the process significantly.

One example of excavation as the treatment method of choice was the Phase II Remediation at the Tundra Mine Site, Northwest Territories, where arsenic and hydrocarbon contaminated soil and waste rock was removed (PWGSC 2015). The amount of arsenic removed through the remediation form of excavation was not mentioned in the literature.

Containment

The containment of contaminants is often chosen over the use of innovative treatment technologies, especially in regards to tailing ponds, landfills or smaller spillages, to save costs and meet minimum guidelines. Containment involves the horizontal or vertical physical separation of a contaminated area to reduce the spreading of pollutants. Vertical containment applications are used to reduce the flow in or out of a contaminated area, whereas horizontal containment prevents the downward flux of contaminants or the physical contact and exposure of the substance to humans and animals. Horizontal containment is also used to reduce the infiltration of precipitation, thereby minimizing the leakage of pollutants. Containment occurs through the installation of cover systems, also called caps, which act as barriers. Cap layers are often composed of different geosynthetic materials, commonly Geomembranes, Geosynthetic Clay Liner, and Geocomposites. Remediation projects within Canada where horizontal capping was chosen as a treatment solution for arsenic contamination included the 16.5 million dollar restoration of the Aldermac Mine Site in Québec. For this site, an impervious covering was placed over a significant portion of the tailings to reduce the supply of water and oxygen, thus preventing the drainage of arsenic-containing mine tailings (Cyr 2008). Any detailed data sets or results in terms of efficacy for the site's remediation implementation are not available at this point. Similarly, Geosynthetic Clay Liners were used at the Montague Gold Mine Site in Nova Scotia as the treatment solution to cap arsenic-containing tailings (Hosney and Rowe 2013). Finally, part of the Phase II remediation at the Tundra Mine Site, Northwest Territories, between 2011 and 2014 included the installation of Geomembranes and Geotextiles within the tailings area containing arsenic (PWGSC 2015).

In cases where vertical containment is required, cut-off walls are often erected. Such technologies include Grout Curtains, Sheet-Pile Walls, Slurry Walls, and vertically installed Geomembranes (Smith et al. 1995). At the Deloro Mine Site in Ontario, an arsenic treatment plant was installed featuring an 80 m concrete underground wall that blocked the flow of groundwater into the Moira River. The groundwater is stored in clay-lined water holding ponds. It is then pumped to the treatment plant where 99.5 % of arsenic found in the groundwater is removed (Noble 2015). The specific arsenic removal procedure used at this point in the remediation process at the Deloro Mine Site treatment plant has not been identified in existing literature.

Dewatering

Dewatering technologies are sometimes used as part of a remediation plan on contaminated sites. The strategy is to impact the hydraulic gradient through pumping in such a way that the migration of the contaminated groundwater can be controlled. Pumping systems may be used, according to (Preene 2012), for hydraulic containment, meaning the groundwater level is intentionally lowered near a contaminated area causing the groundwater to flow towards the centre of a plume and preventing further spreading. In some cases, the groundwater level may be lowered for a contaminated area to allow for excavation of the contaminated soil (Preene 2012). Often the water extracted from the pumping well must undergo chemical treatment before it can be discharged. Dewatering may be used before the disposal or chemical treatment of sludge (MOE 2008). Zheng et al. (2012) explained that dewatering is a crucial part of the disposal of tailings as their water content is generally higher than 70%. Malikova et al. (2016) mentioned that the pre-treatment of tailings with coagulation/flocculation agents is often unavoidable for the dewatering of contaminated water which contains very fine particles. No cases have been identified where dewatering was specifically used for the removal of arsenic, which indicates that other remediation methods are likely more effective in removing arsenic.

2.2.2 Soil and Waste Treatment Technologies

Solidification/Stabilisation

The process of solidification/stabilisation (S/S) has been renowned to be an affordable treatment option for the effective disposal of As containing soil and wastes (Wang and Zhao 2008). Solidification generally refers to the encapsulation of hazardous waste into a high-integrity structure, such as cement or other binding materials. Once the hazardous waste is isolated within the binding material, its migration ability is greatly reduced. Stabilization, on the other hand, is a process where waste and stabilizer are mixed together to achieve an alteration in the waste's chemistry, which is essentially a reduction in toxicity, solubility and mobility (Derghazarian 2010). Both methods are used ex-situ and in-situ. S/S processes are generally less expensive than other arsenic treatment technologies, but their success depends on the valence state of the arsenic which impacts the leachability of the stabilized material (EPA 2002). The S/S processes’ overall performance may be improved by the addition of iron salts (Wang and Zhao 2008). Wang and Zhao (2008) explained that the final waste volume can be increased by >30% for S/S, thus requiring additional disposal space. The efficacy of a new stabilisation technique was studied on arsenic-containing tailings from the Casa Berardi Mine site, located in North-West Québec

(Coussy et al. 2011). The tailings management stabilisation technique was called the cement paste backfill (CPB), which was formed under a low portion of high hydraulic binder mixed with water. Three different binders were tested in their study. The outcome of their study indicated that slag- and Portland cement based CPB released less As than fly ash-based binders. Nevertheless, the fly-ash-based binder stabilized As better at lower pH.

Pyrometallurgical processes

Pyrometallurgical processes are primarily used in the metal mining and smelting industries. Most commonly, minerals and metallurgical ores are thermally treated at high temperatures to create physical and chemical transformations in the treated material. This form of separation is often applied to recover remaining valuable metals. In terms of arsenic, pyrometallurgical treatment is used to recycle high concentrations of arsenic from industrial wastes, metals, or smelters. However, the process may not be suitable to treat soil and waste with low arsenic concentrations (EPA 2002). At the National Smelting and Refining Company Superfund Site, in Atlanta Georgia, arsenic containing secondary lead smelter slag has been thermally treated at high temperatures for metal recovery. Initial arsenic concentrations in the waste feed ranged between 428 to 1,040 mg kg^{-1} (EPA 1999). After the separation, the remaining effluent slag still contained As concentrations between 92.1 to 1,340 mg kg^{-1}.

Vitrification

The process of vitrification involves the high-temperature treatment of contaminated soil and waste. The technique is generally applied in-situ (Meuser 2010). It aims to reduce the mobility of metals by injecting an electric current into the soil or waste which is then heated by a generator. Temperatures usually reach between 1,000 to 1,800 °C (Bradl 2005; Mirsal 2004). As the temperature increases, the treated material melts. Any pollutants not pyrolyzed by the high temperature are incorporated into a chemically durable, leach-resistant, vitreous mass (EPA 2002). The process of vitrification followed by crystallization has been used in the past specifically for the immobilization of industrial wastes (Rincón and Zayas 1994). Vitrification treatment is defined by EPA (2002) as an expensive and energy demanding process that may be preferable to Solidification/Stabilisation in cases where a combination of various contaminants is present. Meuser (2010) explained that the maximum treatable soil depth is about 10 m. During the in-situ treatment the soil should be fairly homogenous to achieve consistent remediation results. Highly concentrated areas, voids, high soil moisture and scrap metal might impact the vitrification method's efficacy (Meuser 2010). Thus, the process has been applied to only a limited number of cases for the treatment of arsenic contaminated soil and waste and documentation is not available at this point. Moreover, off-gases may develop throughout the process which might require additional treatment (EPA 2002; Meuser 2010).

Soil washing/Acid extraction

During the soil washing treatment process, hazardous contaminant concentrations are lowered using particle size separation. This treatment technology has been well established in some European countries including Belgium, Germany, The Netherlands, Switzerland and the United Kingdom, but also North America and Japan (Pearl et al. 2006). The contaminated material is mixed with and washed in a water-based solution that may contain additional chemical additives, such as leaching agents, surfactants, acids, or chelating agents, that enhance the removal of organic matter and heavy metals (EPA 2002). This ex-situ process is established on the principal that contaminants are prone to bind to fine-grained soils such as silts or clays. Once they are bound together, the fine particles together with the wash solution are separated by size from the cleaned coarse grains. They are then further treated or disposed of, depending on the requirements. The cleaned coarse-grained material might be reused as backfill if contaminants were removed or immobilized sufficiently. A pilot study was performed by (Ko et al. 2005) to analyze the acid washing of As contaminated soil with hydrogen chloride, sulfuric acid and phosphoric acid. They determined that the chemical extraction of As was limited for finer particles. The EPA (2002) reported that soil washing/acid extraction has been applied to a limited number of cases to treat arsenic contaminated soils. A soil washing treatability study was performed on contaminated sediment from a wood preservation site in Thunder Bay, Ontario. The initial arsenic concentration of 9.1 mg kg^{-1} of the sediment was reduced to 0.015 mg kg^{-1} (EPA 2002).

Soil flushing

This in-situ technology is similar in its approach to the soil washing process, as organic and inorganic contaminants in the treated soil are extracted under the addition of a water-like solution that may contain chemicals or an organic extractant. By injecting or spraying the solution into or onto the contaminated area, target pollutants are then mobilized by dissolution or emulsification and become part of the flow (EPA 2002). Once the zone of contamination is fully flushed by the injected solution, the then pollutant-bearing flushing solution is extracted through pumping and collected at the surface for further treatment, if it is not reinjected or discharged. CPEO (2017) explained that the effectiveness of soil flushing depends on the type of soil, type of contaminant and the soil moisture content. One disadvantage is that small residuals may be left in the soil from flushing additives. Furthermore, soil flushing can cause the spreading of the contaminant plume beyond the remediation zone (CPEO 2017). According to the EPA (2002) only a limited number of applications are known in which the in-situ soil flushing technology has been used for the treatment of arsenic-contaminated sites. Rhamnolipid biosurfactant-enhanced soil flushing was studied in a column experiment by Wang and Mulligan (2009) to investigate the removal of arsenic (As^{+5}) and heavy metals from a mine tailings sample collected in Bathurst, New Brunswick. Their results showed that a change in arsenic oxidation state did not occur under the addition of rhamnolipids. Furthermore, the study concluded that the simultaneous removal of arsenic and heavy metals could be improved substantially if the treated solution contained 0.1% rhamnolipids. Finally, the initial As concentration in the tailings sample being 2,180 mg kg^{-1} was reduced to 148 mg kg^{-1} after a 70-pore volume flushing (Wang and Mulligan 2009).

2.2.3 Water Treatment Technologies

Precipitation/Coprecipitation

The process of precipitation/coprecipitation is often used in technologies specified for the treatment of arsenic-containing water, including groundwater, surface water, leachate, mine drainage, drinking water and waste water (EPA 2002). Nevertheless, it is also capable of treating other heavy metals besides arsenic. This method is generally applied in combination with pH adjustments, chemical precipitants, or chemical oxidants (FRTR 2017). Chemicals are added to the water and used in the precipitation process to transform dissolved contaminants into an insoluble solid (EPA 2002). Once the solids are formed, they may be removed from the liquid phase by coagulation and filtration. In coprecipitation, soluble contaminants that would have normally remained dissolved in a solution are instead carried out of the solution by a precipitate.

Chemicals and methods that are used for the removal of arsenic are, according to the EPA (2002), ferric salts, ferric sulfate, ferric hydroxide, ammonium sulfate, alum, pH adjustment, lime softening, limestone, calcium hydroxide, manganese sulfate, copper sulfate, and sulfide. Various technologies use a combination of precipitation and coprecipitation to remove arsenic from the water. Wang and Zhao (2008) pointed out that a limitation with lime precipitation is the forming of gypsum. Moreover, additional treatment with ferric may be necessary to reduce As^{5+} to an optimum level. A filtration problem may occur under the use of sodium sulfide for arsenic precipitation, due to the sodium sulfide's colloidal nature (Wang and Zhao 2008). Arsenic precipitation with alum is limited in terms of arsenic removal capacity to pH between 5.5 and 6. The performance for arsenic removal via precipitation with alum is unsatisfactory (Edwards 1994; Wang and Zhao 2008). At the Inco Copper Cliff Smelter in Sudbury, Ontario, a weak acid treatment process was implemented for the precipitation of arsenic as arsenical ferrihydrites under the addition of SO_2 and H_2SO_4 (Taylor 2013). The data that has been published about the Inco Copper Cliff Smelter did not identify the amount of As removed by the precipitation treatment process. Chemical precipitation with acid addition, copper sulfate and filtration was used as the treatment solution for arsenic-containing leachate at the Kidd Mine in Timmins, Ontario, and the Equity Silver Mine in Houston, British Columbia. The treatment resulted in a total recovery of 98% of arsenic at the Kidd Mine and a 95 – 98% recovery at the Equity Silver Mine (EPA 2002). A metal refinery in Fort Saskatchewan, Alberta, used chemical precipitation and filtration for the treatment of arsenic-containing leachate, which had originated from the recovery of silver ores. The available data does not contain information regarding the As removal efficacy of the precipitation and filtration process. At the Giant Mine near Yellowknife, Northwest Territories, ferric sulfate was used in the local water treatment system to promote the precipitation of arsenates.

In addition, a flocculating agent and lime were injected to remove arsenic and other mining-related metals (Fawcett et al. 2015). The treated tailings water had an initial As concentration between 4.7 and 14 mg L^{-1}. After the treatment the remaining As in the settling pond had only a concentration of 0.003 mg L^{-1} and was then pumped to the polishing ponds.

Adsorption/Desorption

Adsorption is frequently used as a process to treat arsenic-containing groundwater and drinking water. During the adsorption process, contaminants adhere to the surface of a sorbent. This essentially leads to a reduction in the concentration of the contaminant in the bulk liquid phase (EPA 2002). The adsorption processes that occur are related to ion exchanges between available charged adsorption sites and charged soluble ions, as well as London-Van der Walls bonding (Vance 1995).

Generally, the removal of arsenite is more challenging than that of arsenate (Bissen and Frimmel 2003b). In order to overcome this challenge, arsenite may be oxidized to form arsenate although the reaction is slow (Wang and Zhao 2008). This reaction can be described as follows:

$$H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$$

Favorable conditions for the effective As removal, being over 90%, are according to Wang and Zhao (2008), arsenate occurrence, a high dosage of the sorbent type used including high surface areas and acidic water conditions. The pre-oxidation step may not be necessary for the adsorption of arsenite if Fe (III) and Mn (III/IV) hydroxides as adsorbent types were used. This is because the hydroxides are capable of adsorbing the arsenite (Wang and Zhao 2008).

The opposite of adsorption is desorption where substances are released from or through the solid's surface (Welch and Stollenwerk 2003). Adsorption differs from absorption because the molecules are taken up from the volume and not by the surface of the mineral. Some applications use prefabricated columns that contain a certain adsorption medium. Contaminated water is injected ex-situ into the column and passes through the adsorption medium where contaminants accumulate on available adsorption sites. Once all sites are filled, the adsorption media may be regenerated or disposed of and replaced by a new adsorption medium (EPA 2002). This process has also been used by in-situ technologies, where the adsorbent is directly injected or embedded into the subsurface, e.g. by permeable reactive barriers (Litter et al. 2014). Common types of adsorbent used specifically in arsenic treatment include activated alumina (AA), activated carbon (AC), copper-zinc granules, granular ferric hydroxide, ferric hydroxide coated newspaper pulp, iron oxide coated sand, iron filings mixed with sand, greensand filtration ($KMnO_4$ coated glauconite), proprietary media and surfactant-modified zeolite (EPA 2002). Factors that may influence the effectiveness of arsenic adsorption performance are, for example, the fouling of the adsorption medium in the presence of solids, organics, silicate, phosphate, the oxidation state of the arsenic, the treated water's flow rate and its pH (EPA 2002; Wang and Zhao 2008). The interference of silicate can be overcome if operating at pH 5. The increase in dosage of adsorbent can eliminate the phosphate's negative effect on adsorption capacity (Zhang et al. 2004).

Das et al. (2011) studied the effects and long-term stability of adsorbed arsenate onto ferrihydrite in uranium mine tailings for the Deilmann Tailings Management Facility of the Cameco Corporation in Northern Saskatchewan. In their experiment, they used batch test methods with a fixed pH of 10, which represented the in-situ conditions in the tailings generated at the mine site in Northern Saskatchewan. They found that ferrihydrite transformation reduced by 2 orders of magnitude for an increase of the As/Fe ratio from 0.010 to 0.018. Furthermore, they concluded that the transformation and dissolution of ferrihydrite and goethite was retarded by arsenic. At the Delora Mine Site, Ontario, arsenic contaminated groundwater is pumped to a treatment plant where ferric chloride is added to a chamber of contaminated water at a 2.5/1 ratio to the arsenic. The ferric chloride is then combined with the arsenic compounds to form a flock that passes further along to an adjacent chamber where a polymer is added, causing the flock to finally settle. The treatment plant removed 99.5% of the arsenic in the contaminated water (Noble 2015).

Ion Exchange

This treatment process removes dissolved metals and other inorganic chemicals from the aqueous phase by exchanging cations and anions between the contaminants and an exchange medium. This process has been used for the remediation of arsenic contaminated groundwater, surface water and drinking water. Technologies usually consist of a reservoir that contains an ion exchange resin or ion exchange polymer as a medium. This resin or polymer is generally made from synthetic organic materials, inorganic materials, or natural polymeric materials (EPA 2002). Wang and Zhao (2008) have mentioned the technologies favourable ability for the removal of As^{5+} from drinking water due to the resin’s resilience. However, the resin’s durability can be greatly impacted if substantial concentrations of sulfate or nitrate are present. The exchange medium used for the removal of arsenic from contaminated water is, according to the EPA (2002), a strong base anion exchanger resin. As contaminated water is passed over a resin bed, where ions in the solution are exchanged with similar ions held electrostatically on the contaminated material. Once the resin's capacity is fully reached, it may be treated and regenerated to be reused or disposed of (EPA 2002). The performance of ion exchange technologies may be impacted by the valence state of an element, as inorganic arsenic compounds, such as arsenite, are generally not removed by ion exchange (EPA 2002; Wang and Zhao 2008). Other factors that may impact the efficacy of ion exchange are the presence of competing ions, fouling, the presence of trivalent iron, and the pH (EPA 2002). Ion exchange is generally more expensive than the use of adsorption processes (Wang and Zhao 2008). Anion and cation resins were used for the removal of arsenic in Vancouver, British Columbia, after a spill of chromated copper arsenate from wood preservation contaminated the surface water. The initial arsenic concentration of 0.0394 mg L^{-1} was reduced to 0.0229 mg L^{-1} (EPA 2002). Mulligan et al. (2005) studied the optimization of As removal from groundwater using an ion exchange process containing of a MnO_2-based oxidizing filter column and a Purolite A-300 anion-exchange resin. They concluded that the studied treatment system was feasible to remove >98% of arsenic concentrations. However, the removal of As^{3+} required a pre-oxidation step. Furthermore, the sorption capacity of the resin declined when the pH increased from 6.5 to 8.5.

Membrane filtration

In this technology, contaminants such as bacteria, salts, or heavy metals are separated from the water by passing the contaminated liquid through a selective barrier known as a membrane. A membrane prevents some of the flow's constituents of a certain particle size from passing through the filter. A critical factor that influences the membrane’s removal capacity is it’s material (Wang and Zhao 2008). Thin film composite membranes are superior to cellulose acetate membranes in terms of As^{3+} and As^{5+} removal (Waypa et al. 1997). The membranes are pressure driven and classified based on the particle size that may pass through the membrane or by the pore size of the membrane (EPA 2002). For example a successful membrane pilot study was demonstrated by Floch and Hideg (2004) for the removal of arsenic concentrations from contaminated groundwater in deep wells. The pilot plant was equipped with a pre-treatment system and a ZW-1000 Zenon membrane module. The initial As concentration between 200 – 300 μg L^{-1} was reduced to drinking water standards (<10 μg L^{-1}). Low-pressure membranes are affiliated with microfiltration and ultrafiltration, during which phase contaminants are primarily removed through physical sieving. Conversely, high-pressure membranes usually refer to nanofiltration and reverse osmosis. These high-pressure processes primarily remove contaminants through chemical diffusion across the permeable membrane (EPA 2002). Both nanofiltration and reverse osmosis are more likely to be used for the removal of arsenic due to the low molecular weight of the arsenic species that are dissolved in water (EPA 2002). Membrane filtration is used for the treatment of contaminated drinking water, groundwater and surface water (Wang and Zhao 2008). The membrane's filtration performance may be impacted by suspended solids, high molecular weight, dissolved solids, organic compounds, and colloids. The performance of the membrane is also affected by the oxidation state of the arsenic, pH, and water temperature (EPA 2002). A pilot membrane filtration study was conducted to remove naturally occurring arsenic from the groundwater in Virden, Manitoba. In the first experiment, Moore (2005) investigated the treatment performance of three different nanofiltration membranes for the removal of arsenic from the groundwater. Only one of the membranes was capable of reducing, at its best performance, an initial concentration of 38 to 44 μg L^{-1} to a concentration of 21 μg L^{-1} (Moore 2005). A different experiment by Moore (2005) tested the effect of MnO_2 pre-treatment in combination with the nanofiltration membranes. The treatment results showed arsenic concentrations of <4 μg L^{-1}. As levels in the Virden groundwater continued to be above the MAC of 10 μg L^{-1}. The city spent $1.8 million to upgrade the water treatment facility in 2009 (Ryan 2012), which now uses peroxidation, ozonation, greensand filtration, membrane filtration and chlorine disinfection (Senyk 2010). Since the upgrade of the treatment facility, As concentrations have been reduced from 28 μg L^{-1} to 13 μg L^{-1} (Ryan 2012).

Chemical Reduction/Oxidation

This form of treatment employs strong oxidizing and reducing agents to chemically treat and convert contaminants to less toxic compounds that are essentially more stable and immobile. The technology may be employed in-situ or ex-situ and has shown to be an effective method for the removal of the soils bulk arsenic content (Wang and Zhao 2008). Oxidizing or reducing agents may be mixed into the soil or injected into the groundwater. Common oxidizing agents used for contaminant treatment include oxygen, ozone, hydrogen peroxide, potassium or sodium permanganate and sodium persulfate (EPA 2013). Reducing agents that are commonly used include sulfur dioxide, phosphate, ferrous sulfate, and sodium (Derghazarian 2010; Wang and Zhao 2008). Pre-oxidation is often used in combination with subsequent processes, such as membrane filtration, to promote the removal of As. Processes involving adsorption/precipitation and anion exchange frequently require the pre-oxidation of As^{3+} to As^{5+} to boost the overall removal of arsenic (Wang and Zhao 2008). The water treatment system at the Giant Mine near Yellowknife, Northwest Territories, used hydrogen peroxide in a pre-oxidation step to expedite the oxidation of arsenic and ferric sulfate to promote the precipitation of arsenate (Fawcett et al. 2015). A sodium hydroxide solution was added to a sandy loam in a case study by Legiec et al. (1997). Between 50 – 70% of the initial arsenic concentration was removed. Approximately 40% of As was extracted from a contaminated forest soil in the pH range between 6 – 8, by using a 0.9 M phosphate solution (Alam et al. 2001).

2.2.4 Innovative Treatment Technologies

Permeable reactive barrier

Permeable reactive barriers (PRBs) are used for the in-situ treatment of both organic and inorganic contaminants. They are capable of providing a long-lasting remediation solution that avoids contaminant migration while remaining energy efficient (Wang and Zhao 2008). The technology consists of a wall that is installed across the flow path of the contaminant plume. Drilling techniques are usually necessary to remove existing aquifer rock and to replace it with the reactive barrier (Litter et al. 2014). The wall is equipped with reactive media that allows water to pass through while simultaneously removing or breaking down the target contaminants by precipitation, degradation, adsorption, or ion exchange (EPA 2002). Some of the treatment media that are used for arsenic removal include, according to the EPA (2002), zero valent iron, limestone, basic oxygen furnace slag, surfactant modified zeolite and ion exchange resin. Litter et al. (2014) explained that the barrier should be made of a material with a high hydraulic conductivity and effectively intercept the flow. Factors that impact the performance of PRBs include the presence of fractured rock, depth of the aquifer and contaminant plume, high aquifer hydraulic conductivity, stratigraphy and barrier plugging (EPA 2002). A pilot application for PRBs was tested at an industrial site in Northwestern Ontario. The media used in the trench barrier type was a mixture of ZVI, surfactant modified zeolite, and ion exchange resin (Baker et al. 1997). The initial As concentration of 0.4 mg L^{-1} was reduced to 0.02 mg L^{-1}. Wilkin et al. (2009) performed a pilot-scale PRB study in 2005, at a former lead smelting facility near Helena, Montana where the groundwater was contaminated with high concentrations of As^{3+} and As^{5+}. The PRB with the dimensions 9.1 m long, 14 m deep and 1.8 to 2.4 m wide contained the medium granular iron. The initial As concentration upstream of the barrier was >25 mg L^{-1} with total As concentrations that varied between 40 and 50 mg L^{-1}. During the two year pilot study As concentrations were reduced to a minimum of 2 to <0.001 mg L^{-1} within the PRB.

Biological Treatment

This developing treatment technology is designed for the biological removal or immobilization of contaminants in waste materials, soil and water. Biological treatment of arsenic consists of ex-situ and in-situ processes, that involve the use of microbial activity to effectively minimize and remediate arsenic through processes such as sorption, biomethylation-demethylation, complexation, coprecipitation and oxidation (Wang and Zhao 2009). Wang and Zhao (2009) described biological treatment processes for the remediation of arsenic-containing soils and groundwater as environmentally compatible and cost-effective. Biotic oxidation of iron by the microorganisms *Gallionella ferruginea* and *Leptothrix ochracea* was studied for its remediation capability of As contaminated groundwater (Katsoyiannis and Zouboulis 2004). Arsenic was effectively reduced from its initial concentration ranging between 0.05 mg L^{-1} and 0.2 mg L^{-1} to lower than 0.01 mg L^{-1}. Deng and Liao (2002) studied the efficacy of mixed cultures including *Thiobacillus ferrooxidans* and *Lepptospirillum ferroxidans* in a biooxidation process for the removal of arsenic from refractory floatation sulfide concentrate. The concentrate was primarily composed of arsenopyrite and pyrite. They demonstrated that 95% of the arsenic could be bioleached in 6 days under optimal conditions. Optimal conditions were defined by Deng and Liao (2002), as 10% culture inoculation, 5% pulp density and a 10 mg L^{-1} silver ion catalyst in an iron-free 9K suspension at a pH of 2 and a temperature of 30 °C.

2.3 In-situ Immobilization of Arsenic by Metal Salts

One method of preventing the migration of arsenic in groundwater is to immobilize the compounds occurring in the dissolved phase. As described in the previous sections (Chapter 2.1 and 2.2.3), arsenic adsorbs onto metal oxides such as iron (III) hydroxide ($Fe(OH)_3$). This process leads to a reduction of arsenic in the dissolved phase as the arsenic compounds are bound to the $Fe(OH)_3$.

A number of adsorption and coprecipitation processes have been studied to determine their effectiveness in arsenic removal (chapter 2.2.3). Laboratory and field scale based research activities indicate that the different chemical iron forms, including zero-valent iron (ZVI) and ferrous iron (Fe(II)), are all strong reducing agents (Bissen and Frimmel 2003b; Driehaus et al. 1998; Ramaswami et al. 2001; Raven et al. 1998). Fe(II) occurring in the groundwater may be oxidized by aeration, thus leading to the formation of iron (III) hydroxides. The slow oxidation rate of arsenite is contrary to the oxidation of Fe(II) to ferric iron (Fe(III)) which occurs under rapid aerobic conditions (Bissen and Frimmel 2003b; Driehaus and Jekel 1993). The stability fields for ferrous and ferric iron species (Fig. 2) indicate that Fe(II) is the more dominant form for a pH range between 5 – 8. Additionally, Fe(III) is only soluble in water if strongly acidic conditions are present. Furthermore, Figure 2 shows that the precipitation of iron oxides is controlled by the pH and the redox potential, and it is reduced in the case of lower pH values.

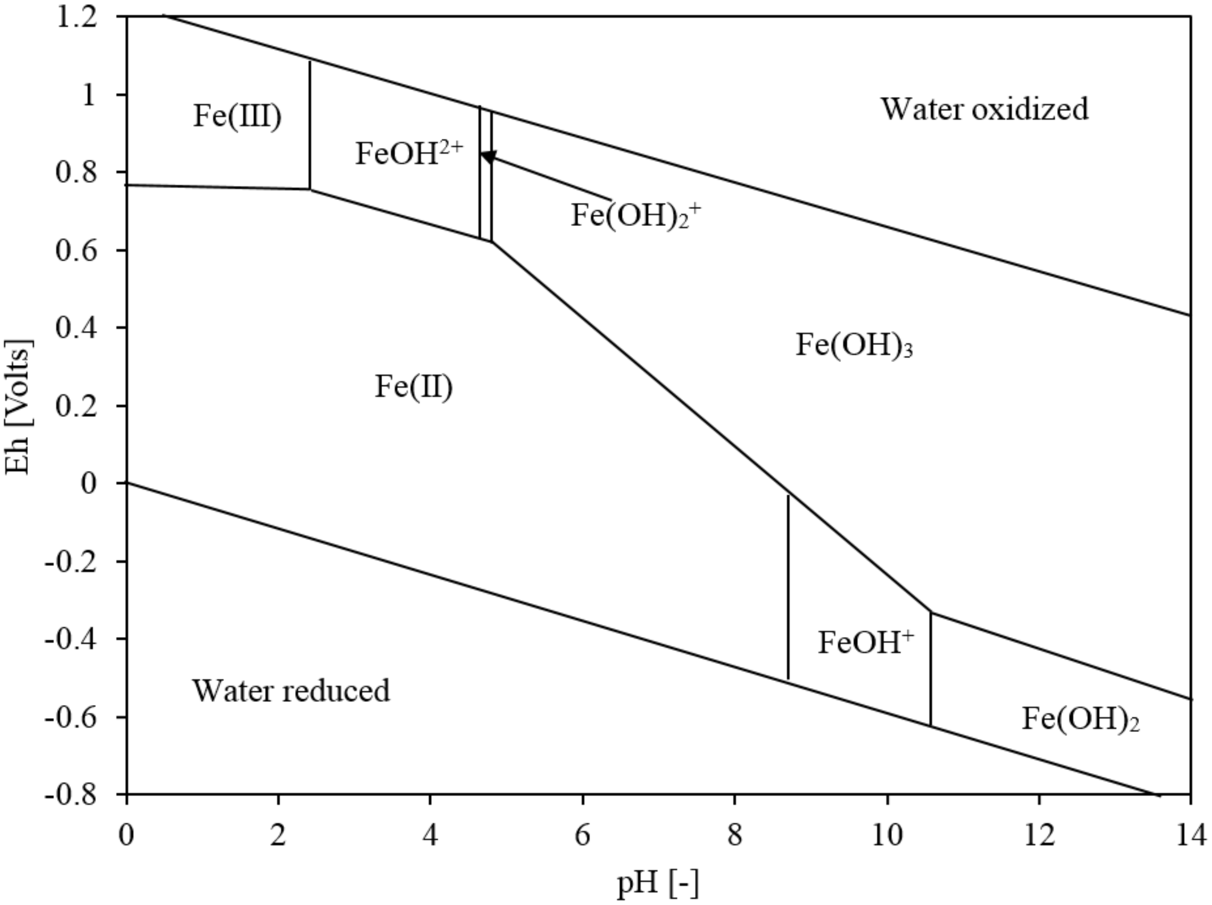

Fig. 2 Eh and pH control on iron speciation, modified from (Hem 1961)

Iron is a common constituent in groundwater. Weathering processes of naturally occurring iron minerals cause the iron to be released and exposed to the groundwater. The successful removal of arsenic by iron precipitation requires that the amount of iron in a solution is always greater than the amount of As (Wilkie and Hering 1996; Scott et al. 1995). A study by Wilkie and Hering (1996) observed the adsorption of As^{3+} and As^{5+} onto hydrous ferric oxide. Different ratios between total arsenic and total iron were examined for the pH range of 4 – 9. The maximum adsorption rate for As^{3+} onto $Fe(OH)_3$ was found for ferric chloride at pH 7 with 0.05 mol As per mole Fe and for As^{5+} with 0.012 mol As per mole Fe at pH 4. Scott et al. (1995) demonstrated the removal of approximately 90% of As with a ferric chloride dosage of 6.5 mg L^{-1}. The arsenic had an initial concentration of 1.6 µg L^{-1}. A total of 82% of As was removed for a ferric chloride dosage of 3 mg L^{-1}. The removal with alum was less effective with only 69% of As removed by a 20 mg L^{-1} alum dosage. As removal of >85% was reported by Meng et al. (2001) by increasing the Fe/As ratio to greater than 40 under the addition of ferric chloride. This ratio was necessary to reduce initial As concentrations with up to 600 µg L^{-1} to <50 µg L^{-1}. Ramaswami et al. (2001) showed in a batch experiment that elemental iron in the form of iron filings was capable of removing up to 95% of As. The initial As concentration of 2,000 µg L^{-1} was reduced to 120 µg L^{-1} under the addition of 2,500 mg iron L^{-1} during a time period between 30 minutes to 3 hours. They further indicated that a maximum of 30 min contact time should be maintained to ensure iron concentrations remain below standards of drinking water. For the injected dosage of 2,500 mg iron L^{-1} the dissolved iron concentration in the vessel reached 195 µg L^{-1} at 30 min and 295 µg L^{-1} at 3 hours, respectively. Pierce and Moore (1982) conducted adsorption studies for arsenite and arsenate at a constant amorphous iron hydroxide concentration of 4.45 mg L^{-1}. Up to 92% of As was removed from the water with an initial As concentration of 1.33 µmol L^{-1} at pH 4. Mamindy-Pajany et al. (2011) studied the adsorption of As^{5+} onto hematite, goethite, magnetite and zero-valent iron under varying physico-chemical conditions including pH and initial arsenic concentration. They determined that the arsenate adsorption was advanced under acidic conditions. The adsorption rate for arsenate onto hematite reached 100% within the pH range of 2 – 11 for the initial As^{5+} concentration of 100 µg L^{-1}. The amount of As^{5+} adsorbed for goethite, magnetite and zero-valent iron was equal to 100% for the pH range 2 – 8 and decreased for higher pH values. The adsorption rate for As^{5+} onto the iron oxides was similar for an increased initial As^{5+} concentration of 500 µg L^{-1} in the pH range 2 – 6, except for the zero valent iron, as 100% of As^{5+}

adsorption was only achieved within the pH range 2 – 5. Krüger et al. (2008) performed a laboratory experiment to test the in-situ immobilization of arsenic in the subsurface by adding ferrous chloride ($FeCl_2$) and oxygen. They showed that both inorganically bound and organically bound As species could be effectively immobilized at a ratio of 0.05 g As/g to 0.19 g As/g Fe. Furthermore, they concluded that a $FeCl_2$ concentration of 2,000 mg per cycle was not sustainable because clogging occurred after four cycles of injection.

2.4 Remobilization of Arsenic

The remobilization of arsenic compounds from the solid phase back into the dissolved phase may occur under certain conditions. The remobilization process involves the solubilization of existing metal-arsenic complexes. It is important to understand the stability of these metal-arsenic complexes to determine the sustainability of the technology.

A desorption test was conducted by Ramaswami et al. (2001) to observe if arsenic removed from the aqueous phase by sorption and precipitation onto iron hydroxide would be permanently bound. They found that no arsenic was remobilized during a 3 hour leaching test. A study by Raven et al. (1998) on adsorption envelopes for coprecipitation of arsenate and arsenite with ferrihydrite showed a release of arsenic at pH <4 and >10, due to the increased solubility of ferrihydrite. Linge and Oldham (2002) measured the changes that occurred in As and Fe partitioning before and after sediment resuspension for a range of differing pH conditions to investigate the resuspension mechanism’s effect on the remobilization of contaminants. They found a correlation between the remobilization of As and resuspension events, during which approximately 20% of the total As was released. Additionally, Saulnier and Mucci (2000) reported the release of As through the resuspension of anoxic sediments in an oxygenated water column.

Meng et al. (2001) evaluated the leachability of arsenic in sludge samples that had previously been used in a household filtration process in Bangladesh. They determined that low concentrations of arsenic were released from the sludge. Shafiquzzaman et al. (2010) examined the stability of the arsenic remaining in the sludge after an iron-based removal process. Different environmental conditions were considered during the stability testing. Laboratory results indicated that desorption might occur for strongly bound As-compounds at high alkaline and low redox conditions. The remobilization of arsenic in water treatment adsorbents under reducing conditions was studied by Jing et al. (2008). Their study concluded that less than 4% of total arsenic was released from iron-based media due to reducing conditions. Remobilization was caused by the reduction of arsenate to arsenite and the reductive dissolution of ferric hydroxides. The conclusion is that a small portion of As might be remobilized under extremely acidic or very strongly alkaline conditions. Nevertheless, the metal-As-complexes seem to be stable for the pH range of 4 – 10. Krüger et al. (2014) studied the remobilization of previously immobilized organically and inorganically As concentrations in a pilot study at a military site in Northern Germany. During the pilot study $FeCl_2$-solution and O_2 were injected into the contaminated aquifer to immobilize the As species in-situ. To study a potential remobilization of the species, the $FeCl_2$ injection of the pilot plant was paused for a 45 day period. Measurements revealed that total arsenic concentrations remained below the initial concentrations and thus that the immobilization was still ongoing, indicating that none of the adsorbed and precipitated arsenic species had been remobilized during the 45 day period.

2.5 Reactive Transport Modeling of Arsenic Mobility

Groundwater modeling offers a simplified representation of a studied subsurface system. The numerical groundwater flow model solves the flow system and is a necessary condition for the solute- and reactive transport analysis. The groundwater flow model includes important physical properties such as flow velocity, which are necessary indicators for how a contaminant plume develops throughout the aquifer system. The three-dimensional transient groundwater flow in a porous, inhomogeneous, and anisotropic medium with a constant porosity is given by the following partial differential equation (PDE) (Rushton and Redshaw 1979):

$$K_x \cdot \frac{\partial^2 h}{\partial x^2} + K_y \cdot \frac{\partial^2 h}{\partial y^2} + K_z \cdot \frac{\partial^2 h}{\partial z^2} + q(x,y,z,t) = S_S \frac{\partial h}{\partial t} \qquad \text{Eq. 1}$$

where (K_x), (K_y) and (K_z) are the hydraulic conductivities in x-, y- and z-direction [LT^{-1}], (h) the hydraulic head [L], (q) the sink and source term [T^{-1}], (S_S) the specific storage term [L^{-1}] and (t) the time [T]. Generally, numerical methods are used to solve the PDE above, in conjunction with necessary boundary conditions. To solve the PDE, partial derivatives are replaced, for example, by the finite difference method (FDM).

Solute transport for groundwater flow is given in the three-dimensional case through the solute transport equation (Eq. 2):

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial L_i}\left(D_{ij} \frac{\partial C}{\partial L_j}\right) - \frac{\partial}{\partial L_i}(v_i C) + \frac{q_i}{n} C_S + \sum_{k=1}^{N} R_K \qquad \text{Eq. 2}$$

where (C) denotes the dissolved concentration of a chemical species [ML^{-1}], (L_i) and (L_j) the distance in i and j-direction [L], (D_{ij}) the hydrodynamic dispersion coefficient tensor in i and j-direction [L^2T^{-1}], (v_i) the seepage or linear pore water velocity [LT^{-1}], (q_i) accounts for the volumetric fluxes associated with the source and sink [T^{-1}], (n) the porosity of the porous medium

[-], (C_S) the concentration for the source or sink [MT^{-1}] and (R_k) the chemical reaction rate formulation [$ML^{-3}T^{-1}$]. Often, this mathematical equation is used in a simplified expression and is referred to as the advection-dispersion equation (ADE) (Bear 1972; Bear and Verruijt 1987; Zheng and Wang 1999).

The solute transport equation can be broken into different terms, where a change in concentration over time (left-hand side of the equation) equals the change in concentration due to dispersion. The dispersion term, in this case, accounts for the two processes, molecular diffusion and mechanical dispersion. The second term on the right-hand side of Eq. 2 represents advection, followed by the third term, which describes external sources and sinks with different solute concentrations, and lastly a term that accounts for geochemical reactions that are necessary for nonconservative solute transport. The different terms of the solute transport equation mentioned above are further explained below.

Advection

Advection represents the transport of a conserved quantity in connected pore spaces along the flowlines of the mean fluid flow. The solute movement in the advective transport process depends on the rate of groundwater flow and its direction. The effective fluid velocity is used to express water flow through the actual pore space. It is defined by the ratio of Darcy velocity and effective porosity,

$$v_e = -\frac{K_x}{n_e}\cdot\frac{\partial h}{\partial x} - \frac{K_y}{n_e}\cdot\frac{\partial h}{\partial y} - \frac{K_z}{n_e}\cdot\frac{\partial h}{\partial z} \qquad \text{Eq. 3}$$

where (v_e) is the effective fluid velocity [LT^{-1}], (n_e) the effective porosity [-], and the Darcy velocity is given by the hydraulic conductivity (K) in x-, y- and z-direction as [LT^{-1}] times the hydraulic gradient in x-, y- and z-direction ($\partial h/\partial_{x,y,z}$) [-]. The three dimensional advective mass flux is expressed as follows:

$$J^{adv} = n_e \cdot v_e \cdot C \qquad \text{Eq. 4}$$

Diffusion

The process of diffusion is a result of mixing caused by the random kinetic movement of particles from an area of high concentration to an area of low concentration in porous media. It is a relatively slow process that occurs even when no hydraulic gradient driven flow is present. It is therefore categorized as a second order mechanism in groundwater because advection and mechanical dispersion are clearly dominant processes. However, it is often the primary transport process in very slow flowing groundwater. The effective diffusion coefficient in porous media is described as the product of the tortuosity and the molecular diffusion:

$$D^* = \tau \cdot D_m \qquad \text{Eq. 5}$$

where (τ) is the tortuosity of the flow paths [-] and (D_m) is the molecular diffusion coefficient [L^{2}T^{-1}]. The diffusive mass flux is then expressed as follows:

$$J_{dif} = -n \cdot D^* \cdot \nabla C \qquad \text{Eq. 6}$$

with (n) as the total porosity [-] and (D^*) the effective diffusion coefficient [L^{2}T^{-1}].

Dispersion

The process of dispersion refers to the mixing that occurs due to the flow; therefore it differs from diffusion by occurring only in flowing water. The process affects all constituents in the water, whether dissolved or suspended.

Mechanical dispersion is a result of local differences in the mean velocity field (Kinzelbach and Rausch 1996), as water particles take different flow paths in a porous medium system, which results in a net spreading of the solute plume. Because mechanical dispersion is strongly flow dependent, it is expected to grow as the flow increases. The mechanical dispersion can be calculated by multiplying the effective velocity with the dispersivity, where the dispersivity is generally expressed as a length. One defines between longitudinal dispersivity in the main flow direction, transversal dispersivity perpendicular to the flow and vertical flow also perpendicular to the main flow direction, as shown in the following equations:

$$D_l = \alpha_l \cdot v_e \qquad \text{Eq. 7}$$

$$D_t = \alpha_t \cdot v_e \qquad \text{Eq. 8}$$

$$D_v = \alpha_v \cdot v_e \qquad \text{Eq. 9}$$

where (α) is the dispersivity [L], and the indices (l, t, v) stand for longitudinal transversal and vertical. Longitudinal dispersivity in the direction of the flow is in general larger than the transversal dispersivity with a ratio of about 10 to 1. The three-dimensional dispersive mass flux is expressed as follows:

$$J_{disp} = -\, n_e \cdot D_{i,j} \cdot \nabla C \qquad \text{Eq. 10}$$

where ($D_{i,j}$) is the dispersion coefficient [L^2T^{-1}]. The dispersion coefficient can further be expressed in tensor form as follows:

$$D_{i,j} = \begin{bmatrix} D_l & 0 & 0 \\ 0 & D_t & 0 \\ 0 & 0 & D_v \end{bmatrix} \quad \text{Eq. 11}$$

The mechanical dispersion term is scale dependent (Kinzelbach and Rausch 1996). Scales often range from microscopic to megascopic. Thus, dispersivity values are often determined through experiments in the laboratory or through field tests. The term hydrodynamic dispersion is often used to combine both dispersion and diffusion.

Sorption Isotherms

Another important transport mechanism for organic and inorganic substances is the adsorption or desorption onto or off of solid surfaces. Adsorption essentially leads to a retardation of the pollutants spreading. The process of adsorption and desorption has been explained in subchapter 2.2.3.

A variety of different mathematical expressions for adsorption and desorption are available in reactive transport models (Wallis et al. 2014). Expressions differ from rather simple empirical relationships, including isotherm equations and distribution coefficients, to more complex surface modeling methods, which additionally account for influencing variables such as changes in pH or solute concentration.

Adsorption isotherms are used to express the equilibrium state for the concentration of the adsorbate in the solution and the amount of solute loading on the adsorbent at a constant temperature.

The simplest approach is a linear relationship shown below, also referred to as the Henry-isotherm which is valid for lower adsorbate concentrations:

$$S = K_d \cdot C \qquad \text{Eq. 12}$$

where (S) is the mass of the solute loading on the adsorbent [MM^{-1}], (K_d) the distribution coefficient [LM^{-3}], often also expressed as the Henry coefficient (κ). The concentration ratio for linear adsorption is simply given by the slope of the adsorption isotherm between the dissolved solute concentration in the solution, and the concentration adsorbed to the surface of the solid. However, the linear Henry-isotherm approach has no upper limit, which leads to the assumption that the adsorption capacity of the system is infinite (Wallis et al. 2014).

More sophisticated approaches are given e.g. through the Freundlich and Langmuir equations. Both expressions are used to relate the amount of solute concentration adsorbed by the solids to the dissolved concentration in a solution and can account due to their nonlinear relationship for the finite adsorption capability of the studied system (Wallis et al. 2014). The empirical Freundlich adsorption isotherm is expressed as:

$$S = K_F \cdot C^m \qquad \text{Eq. 13}$$

where (K_F) is the constant of proportionality also known as the Freundlich constant [L^3M^{-1}] and (m) the constant that controls the nonlinearity of the equation [-]. The Freundlich equation above becomes linear for the case that the constant (m) equals 1, which would then void the upper adsorption limit.

Alternatively, an upper adsorption limit is given through the behaviour of the Langmuir adsorption equation, shown below:

$$S = \frac{QK_LC}{1+K_LC} \qquad \text{Eq. 14}$$

where (K_L) is the partition- or Langmuir coefficient [L^3M^{-1}], (Q) the maximum sorption capacity of the adsorbate [MM^{-1}] and (C) the concentration of the adsorbates in the solution [M^3L^{-1}].

Since arsenic is stable for an infinite period (Davis 1984) As concentrations are not decreased due to decay. Therefore, it is a negligible factor in terms of the modeling of reactive transport of arsenic mobility.

In the past, multiple solute-transport codes have been developed to simulate contaminant transport in the subsurface, such codes include FEFLOW (Diersch 1997), MT3DMS (Zheng and Wang 1999) and FEMWATER (Yeh et al. 1992). These codes are commonly used for the simulation of multi-dimensional solute transport behaviour on the basis of physical transport including advection, dispersion, and diffusion. The reactive process is often only simplified by the codes mentioned above in the form of linear and non-linear sorption and decay. Wallis et al. (2014) explained that the disadvantage of these solute transport codes is that they do not account for coupling and interactions between numerous dissolved species, which would be relevant for arsenic remediation modeling. Thus, it is necessary to add geochemical modeling capable of simulating changes in the water composition due to chemical reactions. Such codes that are commonly used are, for example, PHREEQC (Parkhurst and Appello 1999), MINTEQA2 (Allison et al. 1991), and the Geochemist's Workbench (Bethke and Yeakel 2016). The model PHREEQC is capable of determining reactions in aqueous, mineral, gas, solid-solution, surface complexation, and ion-exchange equilibria (Charlton and Parkhurst 2011). Different geochemical databases are used such as WATEQ4F (Ball and Nordstrom 1991) for the calculation of the reactions. Geochemical models such as PHREEQC (Parkhurst and Appello 1999) incorporate surface-complexation models (SCM) that have previously been used in reactive transport studies to predict interactions for the sorption of arsenic to surfaces (Wallis et al. 2014).

A number of 1D reactive transport models have been developed with PHREEQC to investigate physical and geochemical processes affecting As mobility (Appelo et al. 2002; Charlet et al. 2007; Postma et al. 2007; Stollenwerk et al. 2007). These models have generally incorporated a database with Dzombak and Morel (1990) SCM for the simulation of As adsorption and desorption processes. Additional surface complexation constants for carbonate and ferrous iron on ferrihydrite species have been introduced by Appelo et al. (2002). Appelo et al. (1999) created a geochemical model with PHREEQC, and simulated the in-situ iron removal from groundwater, as studied in a column experiment. Geochemical modeling of arsenic behaviour in a highly contaminated mining soil was performed by Bisone et al. (2016) using the reactive transport code PHREEQC. Ghosh et al. (2003) created a one-dimensional reactive transport model in PHREEQC to model the effects of petroleum hydrocarbons on arsenic solubility and mobility. A one-dimensional model was also developed by Postma et al. (2007) in PHREEQC to determine the controlling parameters for arsenic release into the groundwater of the Red River Flood plain in Vietnam.

A modified UNSATCHEM code (Simunek et al. 1996) was developed by Decker et al. (2006) for the modeling of variably saturated reactive transport of arsenic in heap-leach facilities. Qi and Donahoe (2011) modeled arsenic sorption in the surface by using a dual-site model in MT3DMS (Zheng and Wang 1999). The chemical equilibrium model Visual MINTEQ ver. 3.0 (Gustafsson 2012) was selected by Biswas et al. (2014) to study the role of competing ions in the mobilization of arsenic in the groundwater of Bengal Basin. Sracek et al. (2004) summarized various chemical modeling approaches that are valuable in the study of arsenic-containing groundwater.

The simulation of reactive transport in three dimensions requires the coupling of the groundwater flow model, transport model and reaction model. Available codes that offer these reactive transport capabilities include PHT3D (Prommer et al. 2003), PHAST (Parkhurst et al. 2010) and FEFLOW (Diersch 2002). The code PHT3D (Prommer et al. 2003) requires the flow model MODFLOW (Harbaugh 2005; Harbaugh et al. 2000) to couple the transport model MT3DMS with the reaction engine PHREEQC. PHAST also requires MODFLOW's flow calculations to couple PHREEQC with HST3D (Kipp 1997). Advanced geochemical reaction modeling is made possible in FEFLOW through the addition of the piChem plugin (Wissmeier 2015), which employs the interface version of PHREEQC.

Advanced 2D reactive transport studies for the simulation of As fate have been developed using the code PHT3D. Jung et al. (2009) simulated the physical and geochemical mechanisms that affected As mobility in discharged groundwater in Waquoit Bay, Massachusetts. The study concluded that a SCM approach was superior to an empirical approach in simulating observed As concentrations. Wallis et al. (2010) reported a reaction network in which the sorption of As was represented by an extended SCM from Dzombak and Morel (1990). This included the surface complexation constants for carbonate and ferrous iron on ferrihydrite derived from Appelo et al. (2002), thus allowing the evaluation of the As fate during a deep-well injection trial in the South-West Netherlands. The same reaction network was further used in a numerical model by Wallis et al. (2011) to study As mobility during aquifer storage and recovery (ASR) at a South-West Florida site. The minerals calcite, siderite, pyrite and amorphous hydrous ferric oxide (HFO) were included as equilibrium reactions, while the pyrite oxidation was simulated kinetically. The amount of sorption sites on HFO in the sediment was unknown prior to the modeling, so it was used as a calibration parameter. Krüger et al. (2012) first demonstrated a numerical modeling approach to the simulation of in-situ immobilization of As by iron precipitation at the military site in Northern Germany. The PHT3D based reactive transport model incorporated a simplified reaction network in which As_org and As_i were treated as a single hypothetical As species (As_t). Under this assumption, the adsorption constant for the As_t on iron hydroxide was calibrated on the mean values from a pilot study.

3. Reactive Transport Modeling of an In-situ Immobilization Trial of Organically and Inorganically Bound Arsenic Species in the Subsurface

3.1 Abstract

Improper disposal and handling of arsenic (As) containing chemical warfare agents (CWA) resulted in the contamination of the aquifer at a military site in Northern Germany. Total arsenic concentrations (As_t) in the groundwater at the site are highly elevated and range from 0.081 mg L^{-1} to 8.80 mg L^{-1}. Unlike geogenic arsenic contamination, arsenic at the site is predominantly organically bound and occurs in the form of phenylized As compounds. With the intention to remediate the local groundwater, an in-situ arsenic remediation strategy using bivalent ferrous chloride ($FeCl_2$) was trialled. During a two year pilot study, a total of 2.3 kg of As was able to be immobilized through the infiltration of oxygen and bivalent ferrous chloride ($FeCl_2$). The present study describes the evaluation of the in-situ remediation strategy and the quantification of the in-situ immobilization of organic and inorganic As species using process-based reactive transport

modeling. The developed model framework couples physical and geochemical processes governing the fate of arsenic at the site. Calculations indicate that treatment of approximately 16,000 m^3 of groundwater would be required to remediate inorganic As concentrations to below permissible levels (<10 $\mu g\ L^{-1}$) and organic As species to a minimum of 0.24 $mg\ L^{-1}$.

3.2 Introduction

The element arsenic (As) is an ubiquitous element in the subsurface and, at elevated levels, is known to be carcinogenic. The greatest threat to human health thereby stems from arsenic contaminated groundwater, with geogenic arsenic currently being the single most important groundwater quality problem affecting the health of tens of millions of people worldwide (Fendorf et al. 2010; Rodríguez-Lado et al. 2013).

Additionally, anthropogenic sources such as industrial activities that include wood impregnation, oil refining, gas and coal processing, and military activities can increase As levels in the subsurface (Bergqvist and Greger 2014). Highly toxic As-containing chemical warfare agents (CWA) were tested and produced by the German military during World Wars I and II (WWI & II). Along with other substances, As was present in high quantities in so-called blue-cross CWA (Martinetz 1993). Subsurface contamination by arsenic occurred between and after the wars through the improper disposal and treatment of remaining CWA.

Treatment of arsenic contaminated groundwater is feasible and current options include ex-situ treatment technologies such as coagulation and filtration (Ćurko et al. 2011; Wickramasinghe et al. 2004), sorption techniques, and membrane techniques (Han et al. 2002; Kaartinen et al. 2017;

Sen et al. 2010). These methods are effective in the removal of arsenic, however they can be technologically complex, incur high costs and necessitate the disposal of arsenic-rich wastes.

In view of some of the disadvantages of conventional As removal technologies, in-situ immobilization of arsenic has received greater attention over the last few years. In-situ technologies are aimed at lowering arsenic concentrations in the groundwater through enhanced sorption or co-precipitation of arsenic to metal oxides or sulfides (Druhan et al. 2008; Mettler et al. 2001). Through the injection of iron, ph-adjusted aerated solutions into the contaminated groundwater body, As retention is optimised.

Several batch and field investigations exploring arsenic in-situ removal efficiency using a range of injectants have been trialled (Cui et al. 2010; Miller 2006; van Halem et al. 2010; Welch and Stollenwerk 2001; Xie et al. 2015). In-situ treatment of arsenic contaminated groundwater by aquifer iron coating was trialled by Xie et al. (2015), while Su and Puls (2003) conducted laboratory column tests investigating in situ remediation of arsenic using zerovalent iron and effects of competing ions (phosphate and silicate) on the removal efficiency. In-situ treatment of As contaminated groundwater by injection of compressed air (air sparging) was assessed by Brunsting and McBean (2014). Daus et al. (2008) reported the removal of phenylarsonic acid, which originated in CWA, from groundwater samples by precipitating iron. Holländer et al. (2008) and Krüger et al. (2008) demonstrated the removal of organic arsenical from CWA by the addition of different iron compounds in batch experiments.

Optimization and design of effective in-situ remediation technologies requires a thorough understanding of the fundamental geochemical processes that are induced through the in-situ operation and its effect on the long term immobilization of As. Herein lies the benefit of numerical modeling simulations.

Flow and reactive transport modeling has proven to be a useful tool in quantifying geochemical processes and their effect on arsenic fate at field scale for a range of injection schemes (Krüger et al. 2012; Rathi et al. 2017; Wallis et al. 2011; Wallis et al. 2010).

In this study, the aim was to (1) develop a reactive transport model, which enables the evaluation of the fate of organic and inorganic arsenic during an As immobilization field experiment in an aquifer system at a military site in Northern Germany and (2) to quantify the effectiveness of the injection of $FeCl_2$ to arrest As mobility under the prevailing hydraulic conditions at the site. The developed numerical framework is believed to be transferable to As in-situ operations elsewhere.

3.3 Materials and Methods

Study site

The local subsurface at the military site in Northern Germany contained amongst other chemical species vast amounts of As originating from CWA. Also found were NAPL, explosives, and decomposition products of sulfurous CWA (Krüger et al. 2008). In the course of WWI and WWII, CWA were produced and tested at the military site. At the conclusion of WWII, remaining CWA at the military site were incinerated together with kerosene as an accelerant in open zinc tanks, or they were buried in the ground. This improper disposal and handling of the CWA resulted in the infiltration of high quantities of As into the subsurface, and ultimately the groundwater.

In order to determine the degree of contamination, Holländer et al. (2008) conducted a field sampling campaign in 2005, which indicated As_t concentrations between 0.081 mg L^{-1} and 8.80 mg L^{-1} (Table 1). The As_t was observed to be predominantly organically bound (As_org) and occurred in the form of phenylized As compounds. Additionally, inorganic arsenic compounds

(As_i: As^{3+} and As^{5+}) with an uptake of <10 % of the As_t were discovered. The highest As-levels were found near a former CWA storage bunker (Fig. 3). This As-hotspot has been identified as one of the main sources of contamination and the potential centre of the contaminant plume (Krüger et al. 2014). The contaminant plume initially started near the surface and proceeded to infiltrate deeper into the aquifer system along the groundwater flow path to a depth of approximately 40 m below ground level (m bgl), measured about 130 m away from the centre.

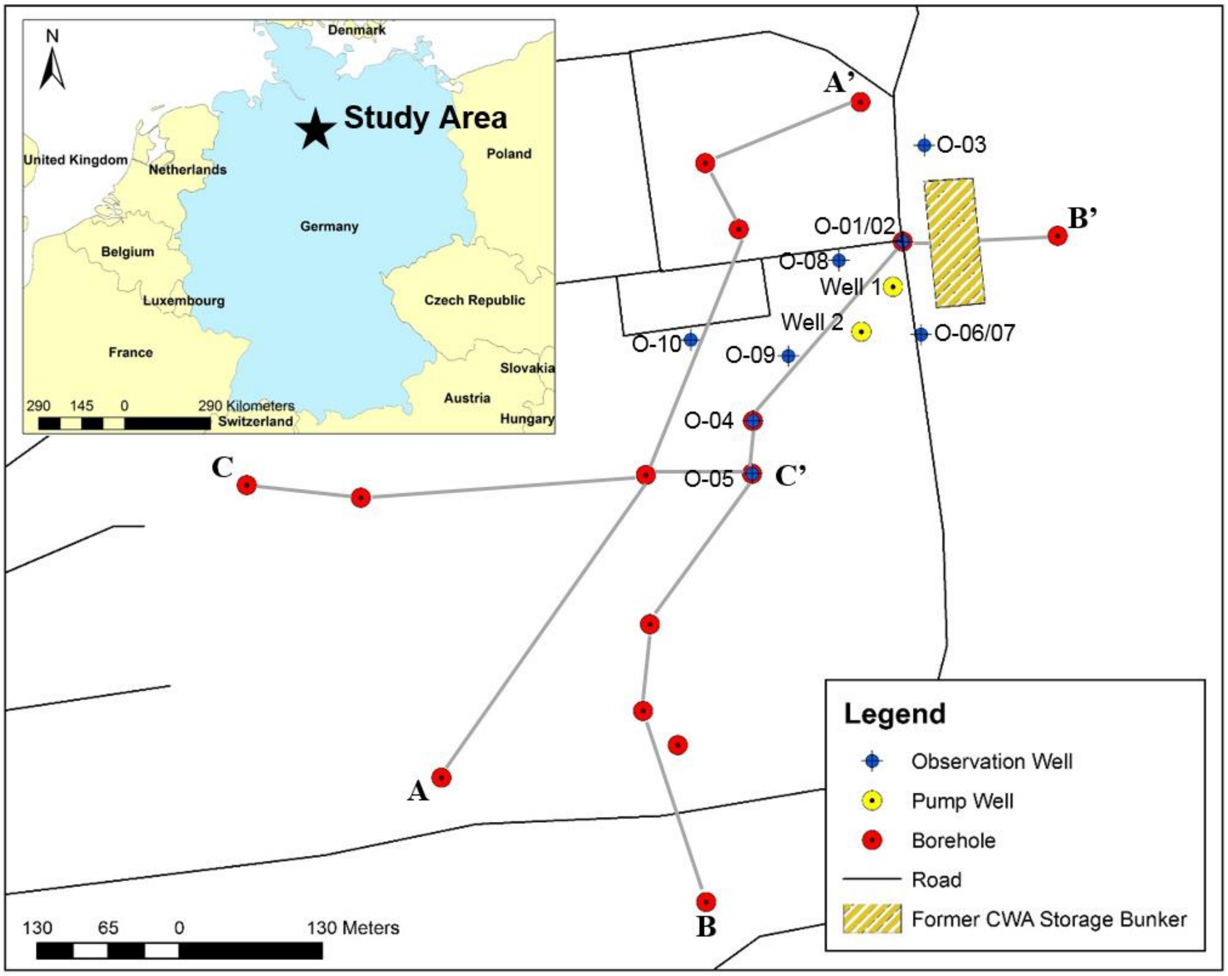

Fig. 3 Plan view of the area of study at the military site in Northern Germany

The hydrogeological conditions for the area of study were derived from two north-south directed cross sections, hinted as grey lines A–A' and B–B' in Fig. 3, as well as the west-east cross section C–C'. Evaluated borehole data indicated a mostly sandy aquifer system with a thickness of approximately 40 m and the ground level located at 80 m above sea level (m asl). Confining silt and marl formations occurred about 40 m asl. The aquifer was roughly divided by two marl lenses acting as local aquitards. Through pumping tests, Krüger et al. (2014) reported a hydraulic conductivity of 4.5×10^{-4} m s^{-1} for the aquifer system. The groundwater level occurred between 5 to 7 m bgl and the flow direction was south-west oriented (Krüger et al. 2014).

A pump and treat facility with a capacity of 190 m^3 h^{-1} has been operating at the site since 1996. Activated carbon is currently used as the treatment method to remove As_org from the contaminated groundwater (Krüger et al. 2014). To increase the overall remediation of the site and further save costs associated to the treatment facility, a pilot plant and well doublet were installed downstream from the CWA storage bunker (Fig. 3) for an in-situ immobilization of As. Preliminary laboratory tests in the form of column experiments were carried out (Holländer et al. 2008; Krüger et al. 2008) and led to the conclusion that the alternating addition of bivalent ferrous chloride ($FeCl_2$) and dissolved oxygen (DO) would immobilize the As_org and As_i in-situ. The pilot plant successfully immobilized arsenic in the groundwater from initial concentrations of around 1.65 mg L^{-1} to less than 0.3 mg L^{-1}. Monitoring results indicated As_i-concentrations of <1 % and 18 % for the As_org fraction in the vicinity of pilot plant (Krüger et al. 2014) After nearly two years of operation, a total of 16,000 m^3 of contaminated groundwater was treated and 2.3 kg of arsenic had been immobilized throughout the span of the pilot study.

Table 1 Summary of the sampling results from the test site (Holländer et al. 2008; Krüger et al. 2014)

Well	As_t [a] (mg L^{-1})	As_org [a] (mg L^{-1})	As^{3+} [a] (mg L^{-1})	As^{5+} [a] (mg L^{-1})	Depth [b] (m)	Temperature [b] (°C)	pH [b] (-)	EC [b] (µS cm^{-1})	Eh [b] (mV)
O-01	8.80	6.08	2.44	0.28	10	11.1	6.79	431	25.5
O-02	0.55	0.36	0.24	0.04	21	10	5.01	207	65.3
O-03	0.77	0.66	0.10	0.01	-	-	-	-	-
O-04	2.37	2.14	0.21	0.02	21	9.8	4.25	216	245.1
O-05	0.081	0.076	0.003	0.002	12	9.7	4.25	283	229.1
O-06	1.11	0.27	0.71	0.13	10	10.4	6.11	227	88.2
O-07	0.15	0.02	0.10	0.03	21	10.0	5.31	210	168.4
O-08	1.66	1.49	0.13	0.04	21	10.7	5.82	301	19.1
O-09	7.76	5.24	2.37	0.15	15	10.3	4.30	252	102.3
O-10	0.36	0.18	0.16	0.02	-	-	-	-	-

[a] As-concentrations were measured during the field sampling campaign conducted in 2005 by Holländer et al. (2008)

[b] Geochemical parameters were determined during a field sampling campaign conducted in 2008 by Krüger et al. (2014)

An additional sampling campaign performed in 2008 intended to determine the geochemical parameters pH, electrical conductivity (EC) and redox potential (Eh) for the observation points O1 to O10 (Table 1). The collected data suggested that the groundwater at the site was mainly acidic with pH ranging from 4.3 to 6.8. Also measured were the electrical conductivity, with values ranging between 207 to 431 µS cm^{-1}, and the redox potential showing values between 19 and 245 mV (Krüger et al. 2014). These values indicated that either iron and manganese reducing conditions or nitrogen reducing conditions occur at the study site. Holländer et al. (2008) confirmed these conditions by reporting Fe(II)-concentrations <50 µg L^{-1} and the abundance of Fe(III). Also measured were sulfate (SO_4) with 42 mg L^{-1}, phosphate (PO_4) with approximately 0 mg L^{-1}, and silica (SiO_2) with 3 mg L^{-1}.

Pilot plant

The pilot plant used for the in-situ immobilization of As has been described by Krüger et al. (2008) as being of similar construction to a subterranean deferrification and demanganeasation plant (Rott et al. 1996). Two bidirectional wells with a screen length of 4 m each were installed downstream from the former CWA storage bunker (Fig. 3). The reason for the short filter screen length was based on the rather low-rated pumping and injection rates (≤ 4.1 m^3 h^{-1}) and to ensure that the water retention time inside the filters was kept short. This design intended to prevent clogging caused by early Fe precipitation near the filter screens and ultimately a reduced well performance. Each well consisted of its own pump and infiltration line, allowing it to either extract groundwater from the aquifer, or if required, to inject groundwater back into it. Well 1 penetrated the aquifer 15 m bgl, while Well 2 was located about 30 m downstream with a depth of 19 m. Groundwater samples were taken from Well 1 and Well 2 prior to the start of the pilot study. These revealed pH values that were contrary to the other observation results' slightly basic conditions. Lower EC values of 196 µS cm^{-1} at Well 1 and 211 µS cm^{-1} at Well 2 were recorded, while both Eh values were within the range of the other observation measurements. The As_t concentration at Well 1 measured 1.3 mg L^{-1} and 2.5 mg L^{-1} at Well 2. Both wells were coupled with a container that included an aeration tank, a degassing tank, and a buffer tank, each with a volume of 500 L. The function of the aeration tank was to either increase or decrease the concentration of dissolved oxygen in pumped groundwater. Following the aeration tank, water was passed into a degassing tank where excess gas bubbles were removed. After proper concentrations were reached, a $FeCl_2$ solution was added to the degassed water and injected back into the aquifer. Also included in the container unit was a buffer tank with the purpose of collecting the pumped contaminant water.

The inaugural operation of the pilot plant was on 22nd October 2008. The pilot plant's operation process involved entirely computerized daily repeating cycles and shut down completely during the night. Both wells opposite of the other either injected or pumped water during its daily cycle. In the case where they had injected water the previous day, they switched to pumping the following day. The precipitation of injected iron took place at some distance away from the wells, as indicated by the absence of clogging. Krüger et al. (2014) explained that the advantage of this system was that treated water was being both injected into and extracted from the same pore space, thus establishing a reactive zone around each well containing a high concentration of $Fe(OH)_3$. The daily cycle of each well was further subdivided into four steps. Prior to each of the four injection steps, the pumping well started 30 min in advance with the extraction of groundwater from the aquifer at 3 $m^3\,h^{-1}$. A fraction of the pumped water (up to 20 %) would be discharged into the adjacent treatment facility. The first injection step commenced with the injection of Fe-enriched water and low dissolved oxygen (DO) at 1 $m^3\,h^{-1}$. Next, water with a low DO concentration was injected at 2.5 $m^3\,h^{-1}$. Thirdly, water with a high DO-concentration was injected at the same rate. The final step involved the injection of untreated water again at 2.5 $m^3\,h^{-1}$. This was necessary to create a buffer zone of water with a lower DO-concentration, thus preventing the precipitation of iron and clogging of the filter when the same well was then switched to pumping the following day.

Reactive Transport Model

To simulate the field trial a reactive transport model was developed using the numerical flow and transport code FEFLOW v7.0 (Diersch 2002), in conjunction with the plug-in piChem (Wissmeier 2015), to allow for the calculation of complex geochemical reactions.

Due to the high computational demand and symmetry existing in the model's geometry along the flow plane, the model domain was created in the form of a simplified rectangular half model with the two bidirectional wells placed along a no-flow boundary (Fig. 4). The minimum necessary horizontal and vertical extent of the model domain is comprised of a 92.5×30 m horizontal area and a vertical thickness of 4 m, which is equal to the length of the filter screens. The model thickness was vertically discretized by three equally spaced layers. The adjacent inflow and outflow boundaries as well as the opposite no-flow boundary were not influenced by the pumping and injection rates. A finite element based mesh with 30,932 nodes was created, resulting in finer discretization around the two wells with a minimal nodal distance of 0.001 m near the wells. Both bidirectional wells were implemented as multilayer well boundary conditions and half pumping and injection rates from the pilot trial were set. These pumping and injection rates were, according to the values mentioned above, from the daily operational cycles. The aquifer fluid flow properties were represented by a constant hydraulic conductivity of 4.5×10^{-4} m s^{-1} based on the pump test. Constant-head boundaries with a resulting hydraulic head difference of 0.5 m were assigned along the inflow and outflow edges of the model, respectively. These conditions characterized the groundwater flow conditions from the area of study.

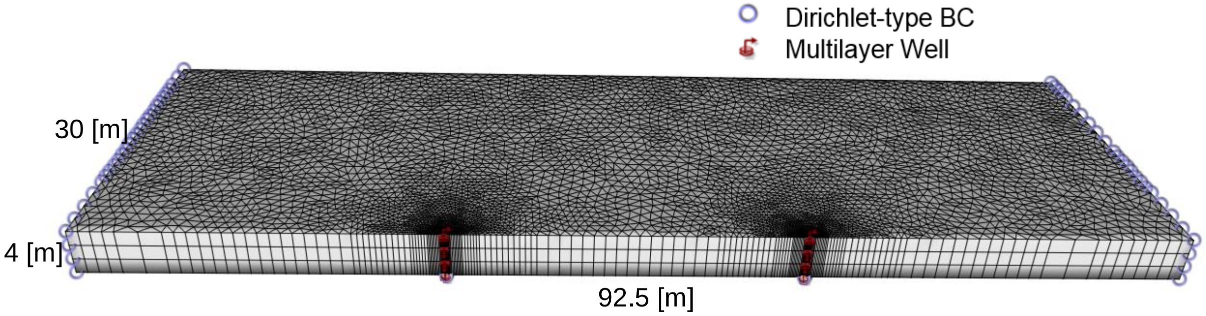

Fig. 4 Schematic representation of the numerical 3 layer model including boundary conditions

As a second model, a full scale model was designed and compared to the 3 layer model (Fig. 4) to evaluate whether the simplified model thickness based on the 4 m filter screen would be acceptable for the simulation of the pilot trial. Additionally, the computational time for each model design was studied. All simulations were run on a network server including an AMD Operton(tm) processor 6176 (4×2.30 GHz, 48 GB RAM) and 64-bit operating system. FEFLOW's reconditioned conjugate-gradient (PCG) solver for flow calculations and the BICGSTABP-type solver for transport with no upwinding were selected. The full scale model with a total of 100,529 nodes was comprised of 9 additional layers, each with a thickness of 4 m. 3 additional layers were placed on top of the 3 layered filter screen domain and 6 layers added below to represent the full 40 m aquifer thickness. The model evaluation was comprised of a simulated tracer test that involved the 30 min injection of a conservative tracer with a concentration of 1 mg L^{-1} at 12 m^3 d^{-1}. This value corresponded to the $FeCl_2$ half injection rate used in the pilot study. Both models' resulting breakthrough curves were then compared and evaluated for discrepancies.

FEFLOW's plugin piChem (Wissmeier 2015) couples the multicomponent reactive capabilities of PHREEQC (Parkhurst and Appello 1999) with the three-dimensional aqueous flow and transport model of FEFLOW (Diersch 2002). This study employed an extended PHREEQC standard database containing the surface complexation constants published in Dzombak and Morel (1990) for the sorption of inorganic arsenic species on hydrous ferric oxide (HFO) (Table 2). To account for the undefined organically bound arsenic species, it was necessary to add the parameter As_org to the database as SOLUTION_MASTER_SPECIES. Furthermore, to enable the binding of the dissolved organic arsenic species to available iron hydroxide ($Fe(OH)_3$) minerals, a SURFACE_SPECIES had to be defined. This linear function is given in Table 2. The precipitation reactions for the forming of the $Fe(OH)_3$ can be modelled via either equilibrium or kinetic expressions. In this study the iron precipitation was modeled kinetically using the rate function from Prommer and Stuyfzand (2005).

Table 2 Surface data implemented for the adsorption of As_i and As_org species on weak binding sites of HFO

PHREEQC Surface Data	log_k
Arsenate [a]	
$Hfo\_wOH + AsO_4^{-3} + 3H^+ = Hfo\_wH_2AsO_4 + H_2O$	29.31
$Hfo\_wOH + AsO_4^{-3} + 2H^+ = Hfo\_wHAsO_4^- + H_2O$	23.51
$Hfo\_wOH + AsO_4^{-3} = Hfo\_wOHAsO_4^{-3}$	10.58
Arsenite [a]	
$Hfo\_wOH + H_3AsO_3 = Hfo\_wH_2AsO_3 + H_2O$	5.41
Organic arsenic species	
Hfo_wOH + As_org = Hfo_wOHAs_org	Calibrated

[a] Surface species defined in (Dzombak and Morel 1990)

First-type Dirichlet boundary conditions and initial conditions were required to solve the governing partial differential equations of the solute transport model. Therefore, constant concentration boundary conditions (CCB) for each concentration species were assigned along the inflow and outflow edges of the model corresponding to measured initial conditions. Additionally, CCB were assigned to each filter screen to account for the injection solution. The initial groundwater concentrations of aqueous components were measured prior to the start of the pilot study by Krüger et al. (2012) and have been summarized in Table 3. The inorganic arsenic species As^{3+} and As^{5+} were summarized by the parameter As_i. The geochemical gradient of the modeled aquifer was represented by 7 zones. This allowed for the simulation of the heterogeneous As concentrations at Well 1 and Well 2. The As concentrations in the 7 zones were linearly interpolated to match the concentrations observed at each well.

Table 3 Native groundwater composition prior to the pilot study (Krüger et al. 2012)

Species	Concentration [mg L^{-1}]	Concentration [mol L^{-1}]	Species	Concentration [mg L^{-1}]	Concentration [mol L^{-1}]
Br	0.11	1.34E-06	Na	17.30	7.53E-04
Ca	16.80	4.19E-04	P	0.03	2.95E-07
Cl	24.29	7.84E-04	SO_4	14.34	1.49E-04
K	3.81	9.75E-05	Si	1.59	2.65E-05
Mg	2.25	9.27E-06	As_org	1.53	2.04E-05
Mn	0.25	4.57E-06	As_i	0.20	2.67E-06

Calibration

The transport parameters of porosity and dispersivity as well as model discretization were calibrated on the data from a conducted field tracer test. The test included the injection of dissolved oxygen (DO) into Well 1 at 3 m^3 h^{-1} and was measured downstream in an observation well (Krüger et al. 2008). In order to reproduce the observed breakthrough curve the longitudinal dispersivity was manually adjusted from 10 m to 0.001 m in one order of magnitude steps for varying porosities between 0.18 and 0.25. The transversal dispersivity was assumed to be 10% of the longitudinal dispersivity.

The unknown nature of the the adsorption amount of the As_org species to the $Fe(OH)_3$ prior to the pilot study had to be calibrated on observed As_org concentrations as constraints. The log_k for the As_org species was used as a fitting parameter. Different log_k values between 5.0 and 7.5 were tested in steps of 0.5. Days 41 to 55 of the pilot study were selected as the calibration period because no operational parameter changes were made to the pilot plant during this 15-day period. Moreover, at this stage of the field experiment the overall processes and conditions had been fine-tuned and any necessary adjustments had been made to the pilot plant. The Fe-dosage was kept at 150 mL/cycle throughout the calibration scenario. The initial As_org concentrations for the calibration scenario corresponded to 1.07 mg L^{-1} at Well 1 and 1.23 mg L^{-1} at Well 2, respectively. The initial As_i concentrations measured 0.12 mg L^{-1} at both wells. Depending on the selected log_k for the As_org species, different amounts of organic and inorganic arsenic complexed on pre-existing Fe(OH)3(a) after the first time-step of the model run. To ensure the simulation of the desired values, the As_i and As_org initial conditions had to be adjusted until they matched the observed values. The observed and simulated values corresponded to the daily averaged concentrations that were measured for the daily extracting well at the start of the pumping phase for a duration of 8 hours. In order to evaluate the difference between simulated and measured daily As concentrations the root-mean-square error (RMSE) was obtained.

Validation

Additionally, a model validation was performed to determine whether the calibrated log_k for the As_org would also produce reliable results at a later stage of the pilot study. The selected validation scenario involved Day 180 to Day 210 of the pilot study. This 30 day period was selected because it included an increase in Fe-dosage from 300 mL/cycle to 375 mL/cycle at Day 195, thus providing some indication of the model's response to the higher iron injection content. Furthermore, the validation scenario shed light on the model's performance regarding the simulation of very low As_i concentrations. Similarly for the calibration scenario, corresponding initial conditions and boundary conditions had to be applied to the model representing the data observed at Day 180 of the pilot study. The initial arsenic concentrations at Well 1 were set to 1.23 mg L^{-1} for As_org and 0.096 mg L^{-1} for As_i. Again, the As concentrations at Well 2 were slightly higher than at Well 1, measuring 1.28 mg L^{-1} for As_org and 0.115 mg L^{-1} for As_i.

3.4 Results

The comparison of the results from the 3 layer and 12 layer model test, indicated that the simplification was reasonable as a close fit between the two simulated breakthrough curves. The simulation of a 24 hour cycle for the full 12 layer model required 26.2 hours of simulation time, however the same 24 hour simulation cycle on the simplified 3 layer model required only 5.6 hours to simulate. Similarly, the average PHREEQC reaction step length was 46.5 seconds on CPU for the full 12 layer model, while the PHREEQC average reaction step length was 13.59 seconds on CPU for the 3 layer model.

Dispersivity and porosity were manually adjusted until the best match between observed and simulated breakthrough curves was found. This was accomplished through setting the porosity to 0.2 in conjunction with a longitudinal dispersivity of 0.005 m (Fig. 5). The transversal dispersivity was assumed to be 10% of the longitudinal dispersivity. Any longitudinal dispersivity values below 0.005 m caused numerical problems in FEFLOW.

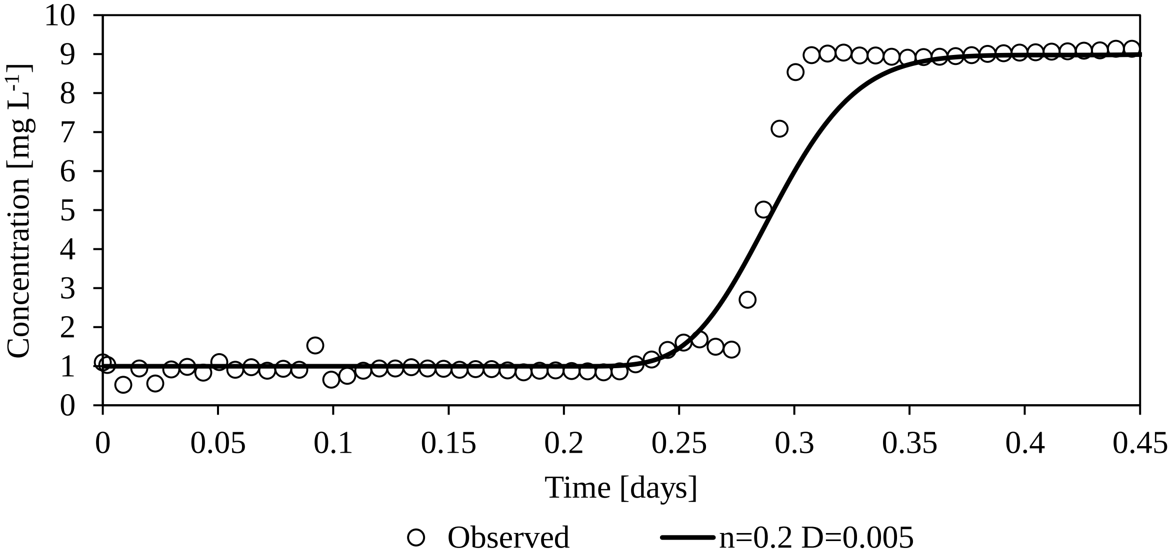

Fig. 5 Simulated vs. observed DO concentration breakthrough curves

The best fit between the observed and simulated As_i and As_org concentrations was obtained by setting the log_k for the organic arsenic to 6.0. The heterogeneous distribution of the initial As_org concentrations at the start of the modeling provided a satisfactory match between observed and simulated values, despite the concentration differential at Well 1 and Well 2. Fig. 6 shows the fit between the numerically simulated values and the observed data points for the 15 day calibration scenario. The RMSE between the observed and simulated data points in Fig. 7 was 39.0 μg L^{-1} for the As_org concentrations and 3.5 μg L^{-1} for the As_i concentrations. The simulated As_i concentrations compared favourably to the observed results from the pilot study for the first half of the calibration period (Fig 6). The numerically simulated concentration reductions for the remaining second half of the calibration period were increasingly lower, owing to the decreased adsorption of As_i. The overall simulation time for the calibration scenario was 91.3 hours.

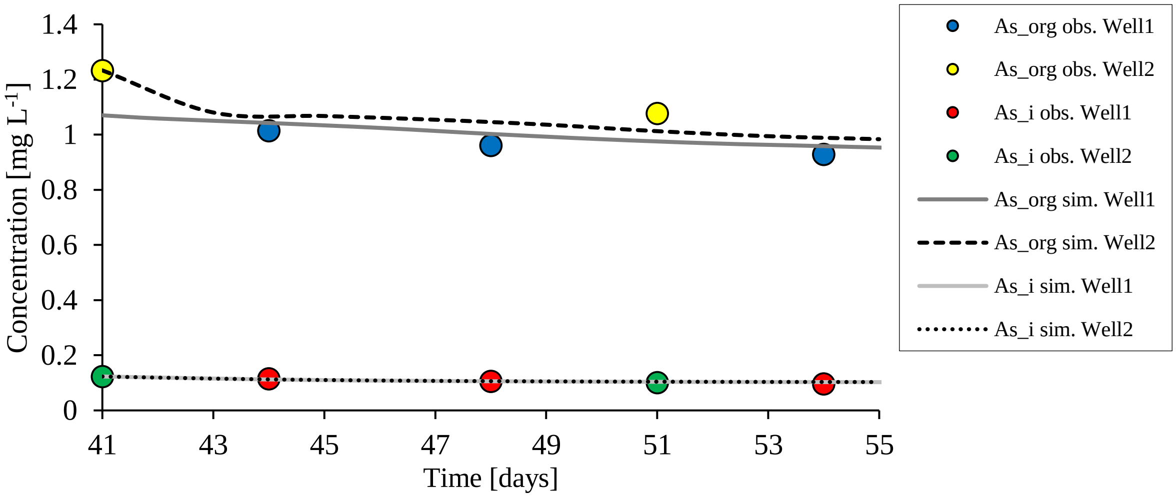

Fig. 6 Simulated vs. observed daily averaged As_i and As_org concentrations for the selected 15-day calibration scenario and a constant Fe-dosage of 150 mL per cycle

The reactive transport simulation of As_i, As_org and $Fe(OH)_3$ species have been displayed for the model cross-section around the two bi-directional wells in Figure 7, showing the initial conditions and the plume development after 5, 10 and 15 days of the calibration period. Both As_i and As_org simulations indicated a plume expansion around each well with lowered concentrations in the groundwater flow direction. In contrast, the $Fe(OH)_3$ concentrations around the two wells increased over time. During the injection of oxygen enriched water the redox potential and pH increased due to the oxidation of the previously injected Fe and the subsequent formation of $Fe(OH)_3$. The natural hydraulic gradient limited the As-immobilization in an upstream direction, so that only a zone with an approximate 4 m radius from the injection gradient reached upstream. The $Fe(OH)_3$ containing ring-shaped zone (Fig. 7) had a radius of approximately 2 m developing around each well. The model simulation of the $Fe(OH)_3$ also succeeded in showing that the injected iron-dosage precipitated along the perimeter of the near circular zone and not immediately in the vicinity of the filter screens. This behaviour was intended to minimize any clogging of the filter screens.

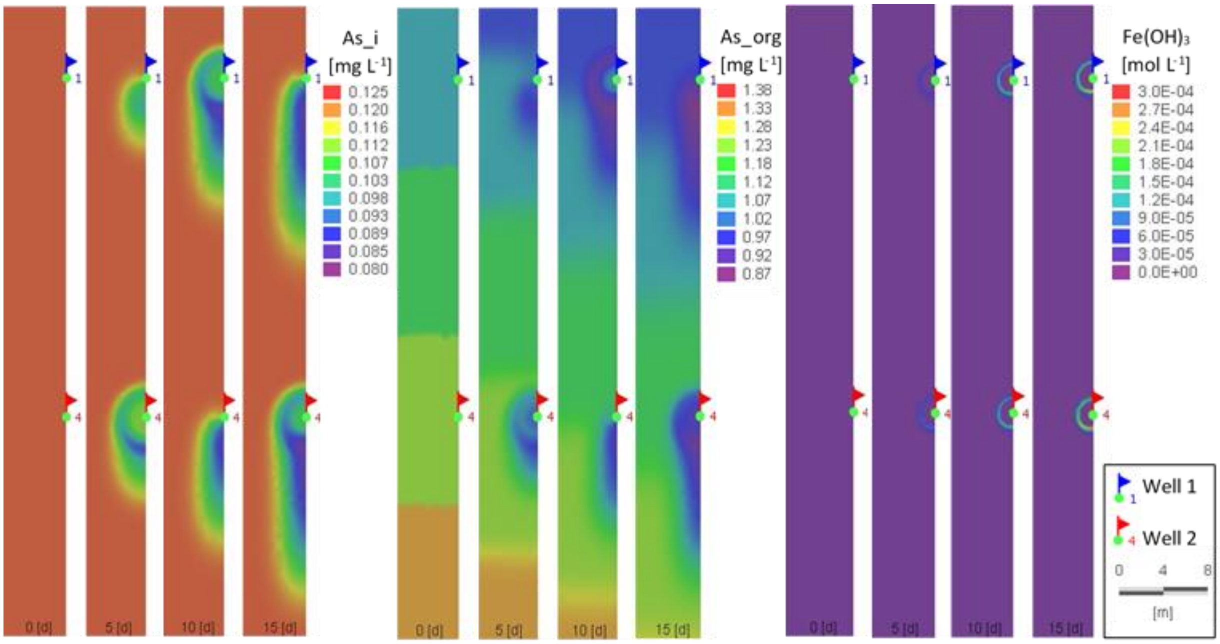

Fig. 7 Plan view of the simulated As_i (left), As_org (centre) and $Fe(OH)_3$ (right) concentrations in the vicinity of the wells, showing the initial conditions and every 5th day of the selected calibration period

The simulated As_org values matched the observed concentration reduction well for the first 15 days of the selected 30 day validation scenario (Fig. 8). However, as the daily Fe-dosage was increased at Day 195, more sorption sites became available and the resulting As_org immobilization rate is simulated higher than originally observed. The general difference (RMSE) was accordingly 125.0 µg L^{-1} between simulated and observed As_org concentrations. Similarly, As_i concentrations were in a good agreement with observed concentrations for the first 10 days of the validation scenario, until the Fe-dosage was increased, which led to a steep reduction of concentrations and thus a RMSE of 24.2 µg L^{-1}. The model run-time included 205.6 hours to simulate the 30 day validation scenario.

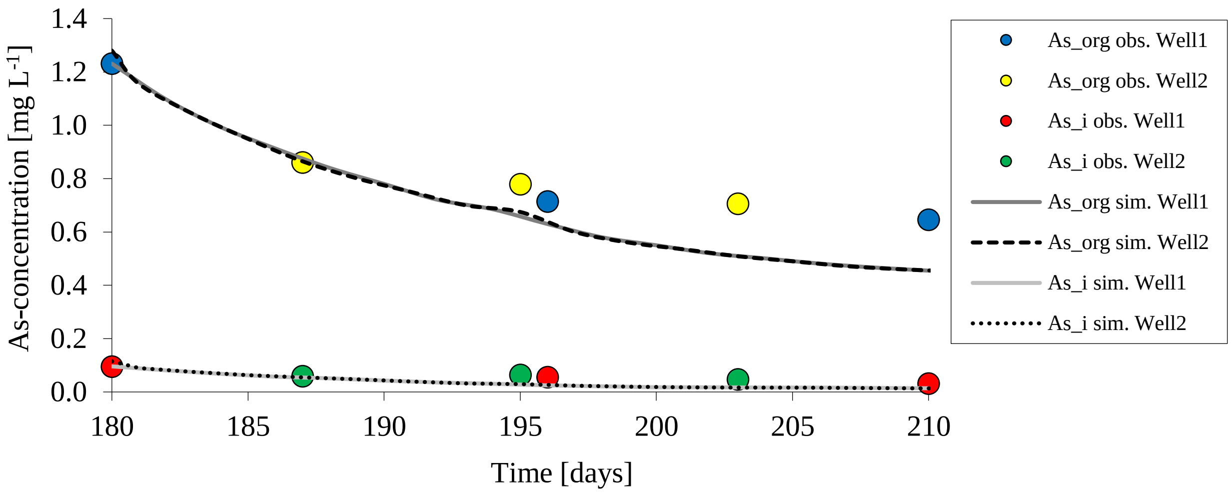

Fig. 8 Simulated vs. observed daily averaged As_i and As_org concentrations for the selected 30-day validation scenario including the Fe-dosage increase from 300 mL per cycle to 375 mL per cycle at Day 195

3.5 Discussion

The simplified representation of the aquifer in the form of the 4 m filter screen was justified by the negligible impact of the very small dispersivity and the short distance that the injectate traveled along the homogenous aquifer base until it was observed at the bottom of the multilayer node. This assumption was further confirmed by the close fit between the breakthrough curves from the 3 layer and full scale model. Moreover, the simplified model's reduced computational demand by a factor of 4.7 allowed for faster execution of longer simulation periods. The use of DO as the groundwater tracer during the field test was assumed to be acceptable as borehole data from within the vicinity of the tracer test suggested the absence of organic matter and thus no interactions with the tracer.

The As_org species previously unknown adsorption parameter log_k was calibrated to 6.0. This selected log_k most accurately represented the adsorption behaviour of the observed As_org species in correlation with the adsorption of the As_i species. The log_k of 6.0 for the As_org species was slightly lower than the log_k of 6.5 from Krüger et al. (2012), since only one hypothetical As species was modeled in their case. Owing to the separate adsorption of both As_org and As_i species to $Fe(OH)_3$ sites, and that each had individual adsorption constants, the constant for As_org had to be lower than 6.5. The validation of the model in the form of a 30 day period was successful in the initial stages of the modeling process, but simulated lower As concentrations for each species with an increased Fe-dosage than originally observed. The likely reason for the accelerated adsorption of both As species during the second half of the model simulation compared to the observed data could be related to heterogeneities in the actual aquifer and different response times between the modeled and observed systems. As both species demonstrated an equally lower simulated concentration trend, the discrepancies are likely not related to the calibrated log_k. If the calibrated log_k were to be adjusted, additional changes to the published adsorption coefficients from Dzombak and Morel (1990) would be necessary as well. However, the log_k values from Dzombak and Morel (1990) were originally determined in batch experiments for pure $Fe(OH)_3$ without the consideration of competing ions. Thus, minor changes to the adsorption constants might be acceptable but are unreliable. Adjusting the kinetics by adhering to the rate law could therefore be a better solution to improve the fit for either species. Furthermore, the exaggerated adsorption of the As_org species might be associated with the very low As_i concentrations (≈ 0 mg L^{-1}). It follows that more sorption sites became available for dissolved As_org compounds as the As_i was primarily immobilized within the reactive zone during the validation scenario. Finally, the As_org fraction was modeled in the form of a single sum parameter, not considering individual As_org compounds that might have been in-absorbable to HFO. This would explain the simulated over-prediction of adsorbed As_org species. Krüger et al. (2014) reported that towards the end of the pilot study As_org stopped reducing, even though the Fe-dosage was increased to 1,000 mL per cycle, which resulted in a Fe/As ratio of nearly 40:1. This implies that the log_k of the As_org species would be ~0 and thus is likely not a constant.

The numerical model simulated the in-situ immobilization of As_i and As_org species in the groundwater and was calibrated and validated for the site specific case of the military site in Northern Germany. These conditions are comparable to many other artificially contaminated military sites where organically and inorganically bound As compounds are present. The extent to which the geochemical model is transferrable to other site specific cases depends on redox conditions and the pH of the present groundwater. Thereby, the native groundwater should have similar geochemical conditions as the observed groundwater from the pilot study, as explained above. At sites where the groundwater is characterized by either strongly basic or strongly acidic conditions, some of the immobilized As might be remobilized (Raven et al. 1998). Also important for the transferability of the model are the As_org species that are directly related to the applicability of the calibrated log_k. Nevertheless, sites with different chemical compositions can still make use of the numerical modeling method introduced in this paper, which has been shown to be effective for the determination of parameters that cannot be directly measured due to the number and complexity of the present species. Generally, future modeling approaches based on the geochemical model developed from the field study are not limited to the initial design of the well doublet and pilot plant. The simulated reactive zones are helpful indicators for decision making in regards to well spacing and potential remediation impact. Well field configuration and parameters can be optimized for future site specific scenarios through numerical simulations to save costs and to compare against other treatment technologies.

3.6 Conclusion

This study presented a successful numerical modeling approach for the in-situ immobilization of organic and inorganic arsenic species with iron precipitation for the case of a contaminated military site in Northern Germany. The simulated inorganic and organic species were calibrated and validated on the observed values from a pilot study with the goal of determining the As_org species corresponding log_k for the adsorption of the organic arsenic species on precipitated iron hydroxide compounds. Setting the log_k of the As_org to 6.0 produced a satisfying agreement between simulated and observed As_i and As_org concentrations. The results indicated that As_org adsorption to HFO sites is nonlinear and that the calibrated log_k for the summarized organic As species is likely not a constant. Furthermore, this study demonstrated how a physical and geochemical process based modeling framework can be used to approximate parameters that cannot be directly measured in batch or field experiments. The geochemical model is transferable to similar case studies that involve arsenic contamination and allows for the optimization and design of the treatment technology.

4. Summary

A numerical model was created to simulate the in-situ immobilization of inorganic and organic arsenic species through the precipitation of ferrous chloride at a highly contaminated military site in Northern Germany. The plugin piChem (Wissmeier 2015) was added to couple FEFLOW`s (Diersch 2002) flow and transport capabilities with the reaction engine PHREEQC (Parkhurst and Appello 1999), thus allowing for the simulation of multicomponent reactive transport. It was shown that a symmetric half model was capable of simulating the in-situ immobilization trial. The data from a tracer test was used for the calibration of porosity and dispersivity parameters.

Necessary boundary conditions were implemented and initial conditions assigned to the model domain. The models adsorption constant (log_k) for the As_org was used as calibration parameter and calibrated on the overserved data from the field trial for a selected 15 day time period during which a constant iron-dosage was maintained. Subsequently, the calibrated model was validated on the observed data from Day 180 to 210 of the field study, including an iron-dosage increase at Day 195. The best fit between observed and simulated As concentrations was given by setting the log_k for the As_org to 6.0. The simulation results showed a $Fe(OH)_3$ containing ring-shaped zone around each well that developed throughout the pilot study as iron and oxygen rich solutions were injected. The iron precipitation along the perimeters of the zones indicated that clogging due to iron precipitation near the filter screens was prevented. During the two year pilot study, a total of 16,000 m^3 of contaminated groundwater was treated and As_i concentrations were reduced to below drinking water standards. However, the As_org species was only reduced to <18% of its initial concentration, despite high Fe/As ratios of 40:1. This indicated that certain As_org compounds could not be immobilized through the in-situ treatment method. It stands to reason that the log_k for As_org is not a constant. The introduced method showed how a large number of compounds difficult to measure can be summarized as one parameter and then be numerically determined. Furthermore, the developed geochemical model is transferable to similar study sites and thus allows for the projection of the in-situ remediation technology for various scenarios.

5. Recommendations for Future Research

Future research is required for the continued optimization and understanding of the in-situ remediation technology. Improving the developed reactive transport model and extending the scope of the work would allow for an enhanced model simulation. Future research could explore the following topics:

(1) A more sufficient method of modeling the recirculation of the pumped solutions could be developed. The initial idea was to use FEFLOW's re-circulation option, the OpenLoop 1.6 plugin for mass concentration transfers. After multiple tests with the collaboration of the FELFOW support team, it became apparent that the OpenLoop and piChem plugin could not be used together as mass balance errors occurred when both plugins were activated. These mass balance errors were triggered by PHREEQC itself. The solution of the chemical reaction in PHREEQC did not converge. It can be concluded that the mass balance errors were not issued by FEFLOW due to factors like discretization. The OpenLoop 1.6 plugin was designed for the application of time-varying concentration differentials in the form of 1-kind boundary conditions between abstraction and injection boreholes. Thus, the coupling of the two codes should be updated so both plugins can function simultaneously. This would eliminate the tedious process of manually entering each distinct 1-kind boundary condition. Additionally, a functional OpenLoop plugin would enable running the model simulations in FEFLOW's Command Line Mode without the graphical user interface. This would expedite the simulation by reducing computational demand.

(2) The implementation of an automated recirculation solution would make possible the simulation of longer modeling scenarios, ultimately leading to automatic calibration through software packages such as PEST (Doherty 2002). Automatic calibration has several advantages over the tedious calibration by hand. These include better fits between

model outputs and observed data, multiple parameter estimation and uncertainty analysis. FEFLOW v7.0 already incorporates a convenient graphical user interface for the use of PEST (FePEST) which could be used for automated calibration and sensitivity analysis.

(3) Some of the simplifications made to the design of the model domain for the reduction of computational demand could have affected the simulation results. The lower simulated concentrations during the validation scenario might have been a result of the simplified 2D model slice consisting only of the 4 m filter screen depth. As the groundwater plume from Well 1 reached Well 2 at approximately Day 26 of the validation scenario an additional decrease in both species' concentrations was given due to the short circuiting of the two wells. Using a more complex 3D model with the filter screens implemented at their actual depths could better indicate whether higher inflow concentrations would result due to a limited short-circuit between both wells.

(4) Additional site investigations would have been beneficial to better characterize the substantially heterogeneous aquifer conditions and to define the geochemical gradient for the model domain. It is crucial that the distribution of initial As_i and As_org species is accurate because the initial conditions significantly affect the immobilization rate. Since the initial conditions prior to the field study have changed significantly, measurements cannot be taken in retrospect. Alternatively, the distribution of initial concentration species could be part of the multi-parameter estimation with PEST.

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