The adsorption potential of arsenic and selenium in soils: A laboratory and pedo-geochemical modelling study

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Abstract

The environmental effects of mine waste recently became of greater interest for environmentalists and researchers in South Africa. Therefore, the rehabilitation of mine waste and tailings and the potential uses of treated mine water became of utter importance. One potential use for treated mine wastewater is as irrigation water for crops. Studies on the possibility of irrigating agricultural fields with treated mine wastewater only focused on the behaviour of metalloid cations present in these waters and the possible contamination of these elements. Consequently, inadequate attention was given to the behaviour and potential contamination of metalloid anions such as Arsenic (As) and Selenium (Se) within these environments.

This study discusses the impact of As and Se in water on soil material replicating soils found in the Witwatersrand gold mining area as well as in the Karoo. The study used batch extractions and geochemical surface complexation modelling by means of the double layer diffusion model to determine the adsorption potential of As and Se on two artificially prepared (soil) substrates at four pH values, representing typical soils found in the Witwatersrand and Karoo areas of South Africa. The prepared substrates represented the average montmorillonite clay and goethite Fe-oxide content in topsoils found in the Karoo region and Witwatersrand tailings. The modelled results were finally compared with experimental data replicating the modelled conditions.

The adsorption of both As (as As^{5+}, AsO_4^{-3} species) and Se (as Se^{6+}, SeO_4^{-2} species) in these substrates decreased with an increase in pH, increasing the possibility of leaching to and contamination of groundwater systems in both mine tailings and irrigated agricultural fields through irrigation with treated mine wastewaters. Due to the high adsorption rates of As within these substrates, the mobility thereof at agronomically high pH values of 7 to 9 in the Witwatersrand substrate or 6 to 9 in the Karoo substrate (or substrates or soils with a similar clay and Fe-oxide content) should not be of major concern. However, this is specific to the conditions and parameters stated in this study. This is also stated without acknowledging the possibility of As accumulation within the mine tailings or soils. Close monitoring should therefore be done to ensure that there is no As accumulation in the soil and that dangerous amounts of As are not taken up by crops or leached into the groundwater systems.

Furthermore, it was shown that Se adsorb less than As and that Se started to sorb less at pH values lower than 5 with respect to As. It was therefore concluded that Se would be more mobile than As at agronomic pH values between 5 and 9 in both the Witwatersrand and Karoo substrates (or substrates or soils with a similar montmorillonite clay and Fe-oxides). The adsorption of Se was however much lower in the Karoo than in the Witwatersrand substrates, possibly due to the much lower montmorillonite clay and goethite content of the Karoo substrates, which do not provide as many sorption sites. The adsorption of Se in the Karoo substrate decreased from pH values >5 and from pH values >7 in the Witwatersrand substrates. The low adsorption rates of Se greatly increases the probability and therefore the risk for Se to leach into the groundwater systems or to be taken up by plants. The irrigation of Witwatersrand and Karoo substrates or soils with a similar montmorillonite clay and Fe-oxides is therefore not recommended.

Keywords: arsenic, selenium, surface complexation, soil substrates

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Declaration

I, Mischke Bouwer, declare that the Master’s Degree research dissertation that I herewith submit for the Master’s Degree qualification Master of Science in Soil Science at the University of the Free State is my independent work and that I have not previously submitted it for a qualification at another institution of higher education.

MBouwer .

Mischke Bouwer

30 January 2020 .

Date

Chapter 1 Introduction

1.1 Background and rationale

There has been a significant increase in the activity and the expansion of mining and related industries during the last few decades. However, this also resulted in the closing and the abandoning of economically unfeasible mines. These increases in anthropogenic activities and closure of mines sensitised environmental scientists on the hazardous effects of industrialisation and mining on all living organisms. This consciousness led to substantial growth in the number of studies on the environmental impacts and rehabilitation of these mines and tailings. Numerous studies have been conducted on the sorption potentials of metalloid cations in soils, while literature on the sorption potential of metalloid anions, especially As and Se in soil, are less common (Kinniburgh et al., 1976; Hiemstra et al., 1989; Hiemstra and Van Riemsdijk, 1996; Fendorf et al., 1997; Grossl et al., 1997; Hiemstra and Van Riemsdijk, 1999; Grafe et al., 2001; Annandale et al., 2002; Grafe et al., 2002; Waltham and Eick, 2002; Hiemstra and Van Riemsdijk, 2006; Luxton et al., 2006; Hiemstra and Van Riemsdijk, 2009; Hansen 2015; Annandale et al., 2017; Favorito, 2017; Favorito et al., 2017a; Favorito et al., 2017b; Favorito et al., 2018; Hansen, 2018; Rahman et al., 2019).

This study focuses on arsenic (As) and selenium (Se). These elements are chemically defined as metalloid anions. It is well known that As and Se can be hazardous or even fatal to both humans and animals when consumed even in small amounts (WHO, 1993; 1996; SANS, 2015). Arsenic contamination is a global concern. Arsenic contaminated sites have been identified in countries such as India, Bangladesh and Australia, where cases of As poising and mortalities have been identified (Meharg and Rahman, 2003; Kapaj et al., 2006; Saha and Ali, 2007; Robinson et al., 2011; Rahman et al., 2019).

The metalloid anions As and Se can be readily mobilised relatively efficiently under a range of different pH and Eh conditions in geochemical environments. Therefore, this has the potential to contribute to larger contamination of groundwater sources and soils. The determination of the adsorption potential and behaviour of As and Se can assist in the understanding of the immobilisation of As or Se contaminated sources under specific pH and Eh conditions. Understanding the adsorption potential of As and Se can be useful for the determination of rehabilitation methodology and impact assessment.

Previous studies on the adsorption of As species (Fendorf et al., 1997; Grossl et al., 1997; Grafe et al., 2001; Grafe et al., 2002; Waltham and Eick, 2002; Luxton et al., 2006; Rahman et al., 2019) focused on the kinetics of As adsorption in the presence of organic carbon and silicic acid. Other studies focused on competing anions, such as sulphates, nitrates and silicates, showing minimal to negligible effects on As and Se adsorption, with the exception of phosphates having a noticeable effect on As and Se adsorption (Dhillon and Dhillon, 2000; Violante and Pigna, 2002; Pigna, et al., 2006; Tuutijärvi, et al., 2012). However, these studies did not necessarily use goethite and montmorillonite as the sorbents. Other comprehensive studies that contributed greatly to the topic of As and/or Se adsorption include the studies of Hiemstra et al. (1989), Hiemstra and Van Riemsdijk (1996), Hiemstra and Van Riemsdijk (1999), Hiemstra and Van Riemsdijk (2006), Hiemstra and Van Riemsdijk (2009), Favorito (2017), Favorito et al. (2017a.), Favorito et al. (2017b.), and Favorito et al. (2018). These studies contributed significantly to this field of study and researched the adsorption of As and Se by using surface complexation models by mainly using MUSIC (multi-site complexation) or CD (charge distribution) model methods. This study will focus on the adsorption potential of As and Se species by the Fe-hydroxide goethite and the montmorillonite clay mineral under varying pH conditions. However, this study is a modelling study and double layer diffusion surface complexation modelling was used.

This study therefore aimed to determine the adsorption potential and behaviour of As (as As^{5+}, AsO_4^{-3} species) and Se (as Se^{6+}, SeO_4^{-2} species) individually in montmorillonite clay and Fe-hydroxide rich substrates at varying pH conditions in an oxidising environment through a batch experiment and to compare results through geochemical modelling.

1.2 Research question and objectives

The research question for this study was: “What is the As and Se adsorption potential of goethite and montmorillonite clay at varying pH conditions?”

The objectives of the study were: 1) To determine the adsorption potential of As and Se individually on two artificially prepared (soil) substrates with different goethite and montmorillonite mineralogical composition as well as varying pH in a batch experiment. 2) To model the influence of pH, in an oxidised environment, on As and Se adsorption in these two substrates with varying goethite and montmorillonite mineralogy.

This thesis is presented in the form of two publishable research paper manuscripts (Chapters 2 and 3, with integrated formatting and with the abstracts and references removed), preceded by an introductory chapter and concluded by a synthesis chapter. References were grouped and are presented as a single section at the end of the thesis. The superfluous text between the two chapters and the literature review has also been excluded.

1.3 Literature review

A metalloid is classified as a chemical element that has intermediary chemical properties between typical metals and non-metals (Britannica, 2017). These metalloids include elements such as antimony (Sb), arsenic (As), germanium (Ge), boron (B), silicon (Si) and selenium (Se) to name a few. This study will, however, only focus on the metalloids As and Se. The metalloid anions As and Se were chosen due to the considerably high concentrations of both As and Se seen in the Witwatersrand mine tailings (Hansen, 2018). These elements can further be classified as heavy metalloid elements along with, e.g. uranium (U), molybdenum (Mo), silver (Ag), vanadium (V), tin (Sn) and chromium (Cr). The elements As and Se behave as anions (negatively charged ions) within geochemical environments. Thus, As and Se are mobile under a more extensive range of naturally occurring conditions, and consequently, have a higher hazard rating than many other trace elements (Sami and Druzynski, 2003).

Arsenic and Se occur as anionic chemical species in soils. These elements recently became relevant in environmental geochemistry because of their toxic interaction with humans and sensitive ecosystems. Metalloids can be toxic or even fatal when consumed in trace amounts (WHO, 1993; 1996; SANS, 2015). Environmental toxicology is a field of research that aims to deal with environmental problems, studying the effect of toxic substances on humans and how to rehabilitate these areas or to slow the contamination of air, soil and water. The concentrations of both As and Se irregularly fluctuate in the environment, partially due to the regional geology (natural source) and as a result of human activity (anthropogenic sources; Sami and Druzynski, 2003). Toxic elements, from both natural and anthropogenic sources, can be mobilised and leached into groundwater, contaminating it, and therefore becoming a risk for possible human and animal consumption and plant uptake (Sami and Druzynski, 2003).

The concentration of As and Se in the soil solution is determined by the sorption processes of these elements. Sun and Doner (1996) and Grossl et al. (1997) propose that arsenate (an As^{5+} ion as $H_2AsO_4^-$) adsorbs onto goethite through a ligand exchange reaction and state that As^{5+} replaces the surface hydroxide (OH^-) groups of the goethite. This adsorption thus tends to decrease with an increase in pH as a result of deprotonation of hydroxides on the surface of goethite and montmorillonite clay creating a negative charge and resulting in As and Se being most mobile at a neutral to higher pH (Grossl et al., 1997).

Although Se is a micronutrient, both As and Se can be hazardous or fatal to humans when consumed in even trace amounts. This is discussed in more detail in sections 1.3.1 and 1.3.2. Arsenic or Se can be consumed through drinking contaminated water or by eating contaminated food- all starting with contaminated soils (as a result of bio-magnification). A complex series of controls, depending on the mineralogy, chemical species and biological processes, determine the toxicity, mobility and fate of As and Se in the environment. High As and Se concentrations in soil and water can be either due to natural sources (weathering of rocks naturally enriched in these elements, volcanic emissions and biological processes) or anthropogenic sources (mining waste, mine tailings and agricultural waste). The principal contributors of As and Se contamination include: Firstly, the neutralising of acid mine drainage (AMD) that immobilises metalloid cations and increases the pH, but consequently mobilises metalloid anions, such as As and Se, thus enabling them to leach into groundwater sources (Hansen, 2018). Secondly, agricultural contaminated soils caused by the historic use of As-based pesticides (Rahman et al., 2019). Thirdly, the presumed success of irrigating agricultural fields with treated mine wastewater (Annandale et al., 2002; Annandale et al., 2017). The latter studies mainly focused on the pH and salinity of the soils and the immobility of metalloid cations but failed to discuss the potential impact of the metalloid anions.

1.3.1 Arsenic

The chalcophile element As (group 15 of the periodic table), is rarely found in its native state due to its affinity to bind with other elements or compounds (Eby, 2004; Davies et al., 2005). Chalcophile elements are group 16 of the periodic table elements that are usually concentrated as sulphide minerals. Goldschmidt (1930) described this group of elements by using the Greek words *chalkós* for copper and *philos* for lover, literally translating to “copper loving” and includes the elements Ag, As, Bi, Cd, Cu, Hg, In, Pb, S, Sb, Se, Te, Tl, and Zn. Arsenic (47th in abundance of 88 naturally occurring elements) has oxidation states that include −3, −1, 0, +3 and +5 and is frequently found as arsenate (As^{5+}) in oxidising conditions and as arsenite (As^{3+}) in reducing conditions (Eby, 2004). This element can occur in different environmental forms such as arsenious acids (H_3AsO_3), arsenic acids (H_3AsO_4), arsenates (AsO_4^{3-}), arsenites (AsO_2^-) and arsine (AsH_3; Choong et al., 2007). The mobilisation and fate of As under both oxidising and reducing conditions are thus sensitive to pH, with Eh and pH controlling the As speciation (Mohan and Pittman, 2007; Figure 1.1).

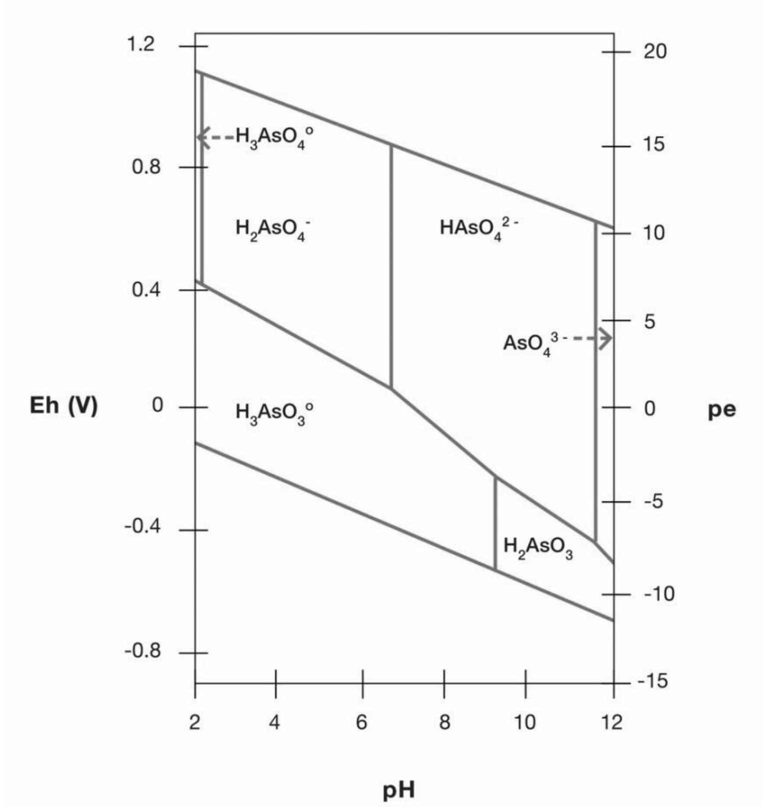

Figure 1.1 pH, Eh (redox potential) diagram for arsenic species at 25°C and 1 bar pressure (Smedley and Kinniburgh, 2002).

The element As occurs naturally in the lithosphere in minerals and rocks and is a critical component in about 568 known minerals (Bowell et al., 2014). These minerals consist of elemental arsenic, arsenides, sulphates, sulfosalts, oxides, arsenate, silicates and arsenites. Some of the most common As-containing minerals include arsenopyrite (FeAsS), less commonly realgar (As_4S_4), orpiment (As_2S_3), marrite ($PbAgSbS_3$), tennantite ($(Cu,Fe)_{12}As_4S_{13}$), and liveingite ($Pb_9As_{13}S_{28}$; Sami and Druzynski, 2003; Smedley and Kinniburgh, 2013). Rocks containing these As-bearing minerals include igneous rocks (such as peridotites, dunite, serpentinite, basalt, gabbro, andesite, syenite and rhyolite), sedimentary rocks (such as shale, phosphorite and coal) and metamorphic equivalents of both these mentioned igneous and sedimentary rocks (Sami and Druzynski, 2003). The As concentration in these rocks are negligibly low and would only be concentrated through either natural chemical processes or anthropogenic processes such as mining.

Arsenic is an extremely toxic metalloid, and dangerous concentrations (discussed later) of As can be found in both natural and wastewaters worldwide (Duker et al., 2005; Choong et al., 2007). The contamination of As in water sources is a major environmental problem and many countries worldwide are affected by As contaminated groundwater (Sami and Druzynski, 2003; Smedley and Kinniburgh, 2013). This contamination can originate from the mobilisation of As through several different sources such as natural chemical weathering, biological activity, geochemical reactions and volcanic eruptions. Anthropogenic sources can include mining (mine tailings, refining and smelting), agricultural pesticides, herbicides, fertilizer and combustion of fossil fuels (Mohan and Pittman, 2007). Throughout the decades of industrialisation, these activities continuously transferred As from the geosphere to the biosphere, where it creates a potential hazard for humans and animals. The toxicity of As is, therefore, a critical environmental issue, since even trace amounts can be carcinogenic, mutagenic and teratogenic (National Research Council, 1999; 2001).

Although small amounts of As contamination in water and soils are normal, the toxicity problem is aggravated by human activities, especially due to a lack of strategies in the management of mining, industrial and agricultural waste. The World Health Organisation (WHO, 1993) guideline value for the maximum As in drinking water was reduced to 10 µg L^{-1}. The soil screening value (SSV) of the amount of As that can be present in a soil, protective of human health and water resources (SSV 1), is <5.8 mg kg^{-1} (Department of Environmental Affairs, 2008). Lastly, according to the South African water quality guidelines, the maximum concentration of As in irrigation water, for long term use, is 0.10 mg L^{-1} (Holmes, 1996). Sami and Druzynski (2003) state that “Arsenic has been associated with skin damage and problems (Bowen’s disease, hyperpigmentation, depigmentation, keratosis, skin cancer), circulatory system problems (peripheral vascular disorders) and an increased risk of internal cancer.” Human consumption of 0.6 mg As kg^{-1} soil per day can thus be lethal (Ratnaike, 2003).

Traditional removal or remediation methods of As from contaminated water include oxidation, precipitation, coagulation and flocculation, membrane filtration and separation, iron precipitation and biological remediation (Mohan and Pittman, 2007). Bowell et al. (2014) state that “despite the substantial body of literature, research on As is continuing, and many recent papers have focused on groundwater with little interconnection to understand the fundamental source(s) of As, its variable speciation in both solid and aqueous form and its interaction with the biosphere.” Even less research was done on the less traditional As removal mechanisms through adsorption and ion exchange, particularly in different soils (Mohan and Pittman, 2007). Sequestration of both As and Se in soils is therefore correspondingly used as a waste management method, whilst guarding against the concentrations thereof becoming hazardous (Sami and Druzynski, 2003; Department of Environmental Affairs, 2008).

1.3.2 Selenium

The element Se (with an abundance of 0.05 mg kg^{-1} in the earth’s crust) is highly mobile in oxidising geochemical environments and can be mobilised in natural waters (Rovira et al., 2008). Selenium contamination originates from both natural and anthropogenic (agriculture, combustion of fossil fuels, nuclear fuel waste and mining activities) sources (McNeal and

Balistrieri, 1989; Rovira et al., 2008). The primary natural source of Se in solution is the Se released from sulphides and metal oxides. Selenium in soils, is the most mobile in irrigated agricultural fields located in semi-arid environments. In these areas, Se is thus plant available and enriched in groundwater (Plant et al., 2005).

Similar to As, Se is geochemically a chalcophile element with chemical and physical properties of a metalloid but can also be described as a non-metal, with a chemical behaviour similar to that of sulphur (Eby, 2004). Selenium (70th in abundance of 88 naturally occurring elements in the earth's crust) has oxidation states which include -2, 0, +2, +4 and +6. The mobilisation and type of species are therefore pH and Eh dependent (Figure 1.2). Selenium frequently occurs as selenate (as a Se^{6+} ion, SeO_4^{2-}) and selenite (as a Se^{4+} ion, SeO_3^{2-}) compounds in oxidising conditions (McNeal and Balistrieri, 1989; Seby et al., 2001).

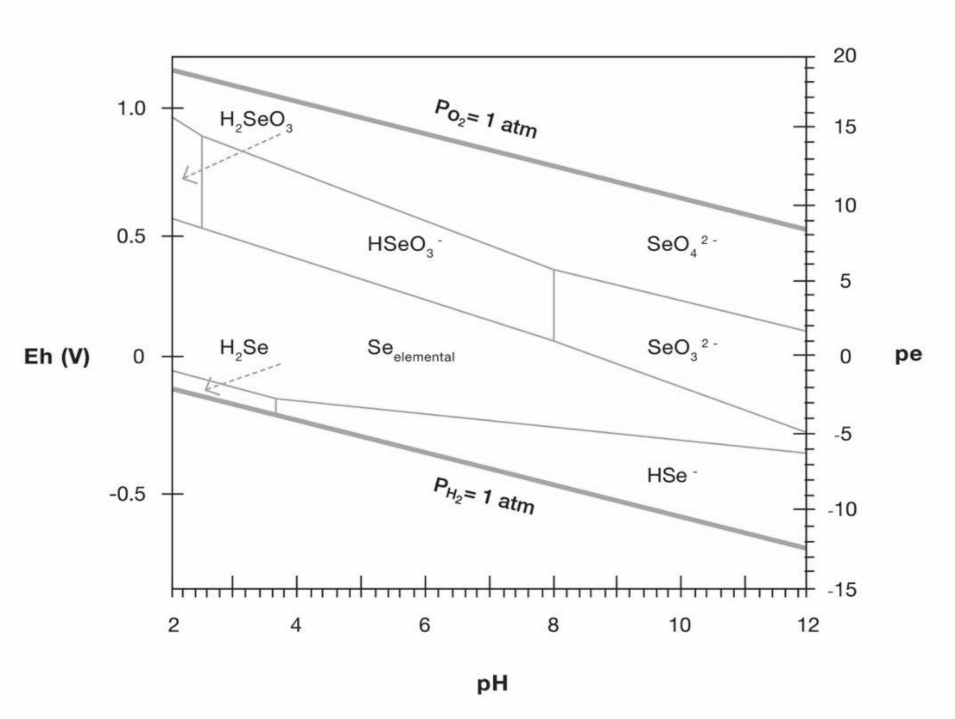

Figure 1.2 pH, Eh (redox potential) diagram for selenium species at 25°C and 1 atm. pressure (Ralston et al., 2008).

Selenium concentrations have increased in the environment due to increased human activity and industrialisation. These activities include mining (such as the mining and processing of base metals, gold, coal and phosphate) and the manufacturing and use of detergents, glazing, paints, ceramics, photocopying and pharmaceuticals (Plant et al., 2005).

The toxicity of Se is much more complex than that of As because Se is a micronutrient that is essential for human and animal health, but in trace concentrations (Davis et al., 2013). Both Se deficiency (<40 µg day^{-1}) and toxicity (>400 µg day^{-1}) can be hazardous or even fatal to human health (WHO, 1996). In contrast to As, very little attention is focused on the toxicity of Se. The WHO guideline for Se toxicity in drinking water is <0.01 mg L^{-1} (WHO, 1996) and according to the South African water quality guidelines the Se standard in irrigation water is <0.02 mg L^{-1} (Holmes, 1996). Unfortunately, no South African soil screening values or guideline maximum amounts of Se in soil could be found and is therefore probably yet to be determined. According to Dutch ecologists, the MPA (maximum permissible addition) threshold of Se is 0.11 mg kg^{-1} (Vodyanitskii, 2016). Sami and Druzynski (2003), in a study on the spatial distribution of naturally occurring arsenic, selenium and uranium in groundwater in South Africa, state that excess Se consumption in humans can cause discolouration of the skin, deformed nails, extreme tooth decay, loss of cognitive abilities and more. The effects on livestock include copper deficiency, thyroid disturbance, cardiac problems, bone and joint corrosion, etc. (Sami and Druzynski, 2003).

Selenium, similar to As, occurs naturally in the lithosphere as minerals and in rocks. According to Sami and Druzynski (2003) minerals containing Se consists mostly of sulphides such as galena (PbS), arsenopyrite (FeAsS), pyrrhotite ($Fe_{1-x}S$), marcasite (FeS_2), chalcopyrite ($CuFeS_2$), pyrite (FeS_2) and sphalerite (ZnS). The overall Se concentrations in rocks are deficient for human health, especially in igneous rocks. The Se concentration in sedimentary rocks is also low and is mainly found in clay-rich rocks. Larger concentrations of Se are found in uranium-rich rocks and volcanic sedimentary rocks (Favorito, 2017; Favorito et al., 2017). Little data is available for Se in metamorphic rock because Se is not mobilised during geological metamorphosis (Sami and Druzynski, 2003).

1.3.3 Sorption

The term sorption is used to describe the removal of a solute from a solution to a solid phase (Jenne, 1998). This phenomenon is significant for controlling the fate and transport of trace elements and nutrients in soil. Understanding the importance and control of sorption on elements can be of great value in various fields, such as controlling the mobility (transport) or immobility of contaminants and plant nutrients, waste management strategies and geochemical prospecting (Sami and Druzynski, 2003). To fully comprehend the term sorption, a few essential terms will be elucidated here.

The term sorbate (or adsorbate) refers to the material accumulating at a solid phase and adsorptive signifies the solute (the ion in solution) that has the potential to sorb onto the solid phase. Sorbent (or adsorbent) denotes the solid phase where the sorbate accumulates or onto which the sorbate sorbs (Jenne, 1998). Sorption can thus be divided into two types: adsorption or absorption. The term adsorption refers to the sorption of the sorbate on the solid's surface, while absorption refers to the diffusion and sorption of the sorbate into the structure of the solid phase (Jenne, 1998; Figure 1.3).

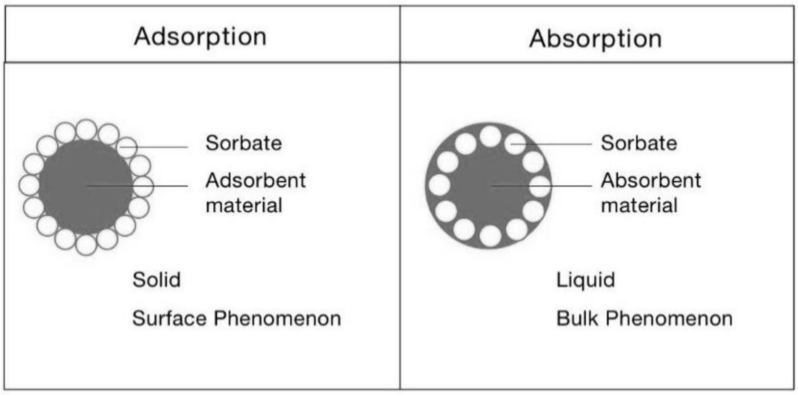

Figure 1.3 Elucidation of the terms adsorption, absorption, sorbate and adsorbent (Jenne, 1998).

1.3.3.1 Fe-oxides and montmorillonite clay as sorbent

This study used an oxide and a clay as sorbents, the solid phase onto which sorbates adsorb. Goethite, a Fe-hydroxide, was selected as the oxide sorbent, while montmorillonite was selected as the clay sorbent. Both the Fe-oxide and the clay act as extremely good sorbents, especially for pH-dependent adsorption reactions (Dzombak and Morel, 1990; Sami and Druzynski, 2003; Plant et al., 2005). The process of pH-dependent adsorption relates to the temporary sorption capacity of a substrate, due to a pH-dependent charge of the sorbent. This adsorption, therefore, relies on the overall charge of the sorbent as a result of the pH and implies that an increase in pH would result in decreasing adsorption due to increased negative adsorption sites (Illes and Tombacz 2006; Jeppu and Clement, 2012). This means that pH-dependent adsorption is completely reversible and could be managed by regulating the sorbent pH (Balistrieri and Chao, 1987). The pH-dependent charge of the sorbent results due to the protonisation (at pH <7) and dissociation (at pH >7) of hydroxide groups on the sorbent's crystal structure. The overall effect would thus be that at a low pH more H^+ ions would be in solution, resulting in the H^+ binding to the OH^-, creating more positive charges on the surfaces of the sorbents. In high pH environments, with less H^+ in solution, the H^+ ions will dissociate from OH^- ions, creating more negative charges on the sorbent surfaces (Dzombak and Morel, 1990; Figure 1.4). Both goethite and montmorillonite have a crystal structure with OH^- on the surfaces, and will thus be subject to pH-dependent adsorption. However, the effect of pH change on the adsorption to montmorillonite will not be so pronounced, since the charge of montmorillonite is primarily permanent due to substantial isomorphic substitution and the small fraction of exposed hydroxide groups on its surface (Dzombak and Morel, 1990). Conversely, the effect of pH change on the adsorption to goethite would be quite large, since goethite has practically no isomorphic substitution to create a permanent negative charge and therefore almost all the sorption sites would be due to pH-dependent charge (Dzombak and Morel, 1990).

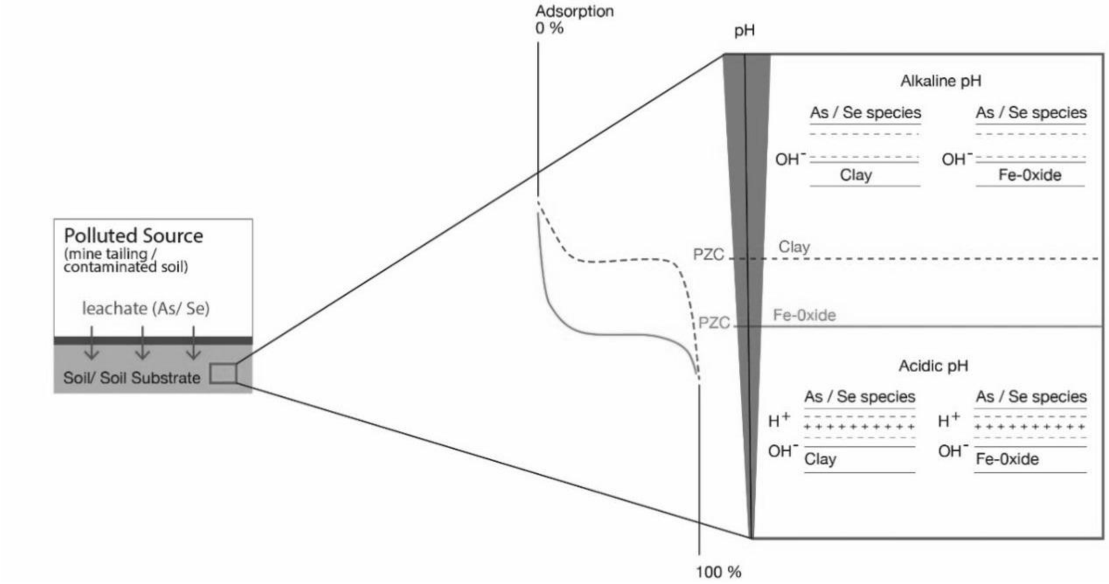

Figure 1.4 Adsorption of As or Se by montmorillonite clay or Fe-oxides, through surface charges, in relation to pH (Dzombak and Morel, 1990).

1.3.3.2 Adsorption of arsenic by oxides and clays

Metal oxides and clay minerals play a significant role in adsorbing and thus minimising the solubility of As in different environments, resulting in a localised reduction of As contamination sites, especially in old mine tailings and dumps.

In oxidising conditions, As (as arsenate, As^{5+}) will be strongly adsorbed at low pH and will slowly desorb as the pH increases (due to the repulsion between the negatively charged sorbate surface and the anion), creating a non-linear pH-dependent isotherm (Plant et al., 2005; Figure 1.5a). Arsenic shows the same pH-dependent adsorption trend from both oxides and clays. The lower adsorption of As^{5+} at a higher pH (pH >8) in oxidising conditions is of significant environmental concern. In reducing conditions As, as arsenite (As^{3+}), decreased adsorption occurs at both low (pH <5) and high pH (pH >9) levels and is thus only strongly adsorbed between a pH of 5 to 9, where the sorption reaction seems to be almost pH-independent (Plant et al., 2005; Figure 1.5b). This study, however, focussed only on the sorption of As in oxidizing conditions.

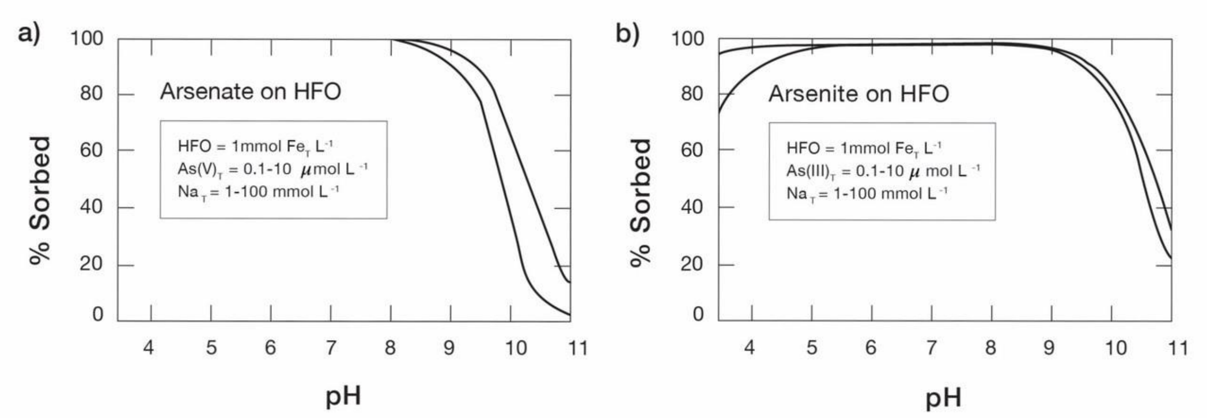

Figure 1.5 a) Calculated As species adsorbed in an oxidised environment; b) Calculated As species adsorbed in a reduced environment (Plant et al., 2005).

This adsorption of As onto the surface of oxides and clay minerals and the different thermodynamics of different geochemical environments are imported into geochemical modelling programs, such as PHREEQC and Geochemist's Workbench, enabling rapid calculations of As adsorption and mobility in geochemical environments (Albarede, 1996; Parkhurst and Appelo, 2013). These calculated results can be used to establish if the role and effect of the oxidation state and pH on As adsorption is significant and thus can be used to indirectly establish the As solubility and mobility.

1.3.3.3 Adsorption of selenium by oxides and clay minerals

Contrary to As, Se^{4+} (the reduced species of Se, selenite) is more strongly adsorbed with Se^{6+} (the oxidised form of Se, selenate) being less strongly adsorbed by metal oxides and clays, and therefore tends to be more mobile (Figure 1.6). Selenium (as selenate, Se^{6+}), in oxidising conditions, and at approximately neutral pH, is more weakly adsorbed and a decrease in adsorption can start at a pH >5 and will increase with an increase in pH. Se (as selenite, Se^{4+}) in reducing conditions will only start to desorb at a pH of around 7 and selenite adsorbs much more strongly than selenate (Figure 1.6; Balistrieri and Chao, 1987; Plant et al., 2005). The adsorption of Se is therefore also Eh and pH-dependent. The Eh and pH, together with the Fe-oxide and clay content of the soil, therefore determines the mobility and bioavailability of Se. Selenium is most adsorbed at a pH of 3 to 5, with the adsorption decreasing and mobility increasing with an increase in the pH (Plant et al., 2005).

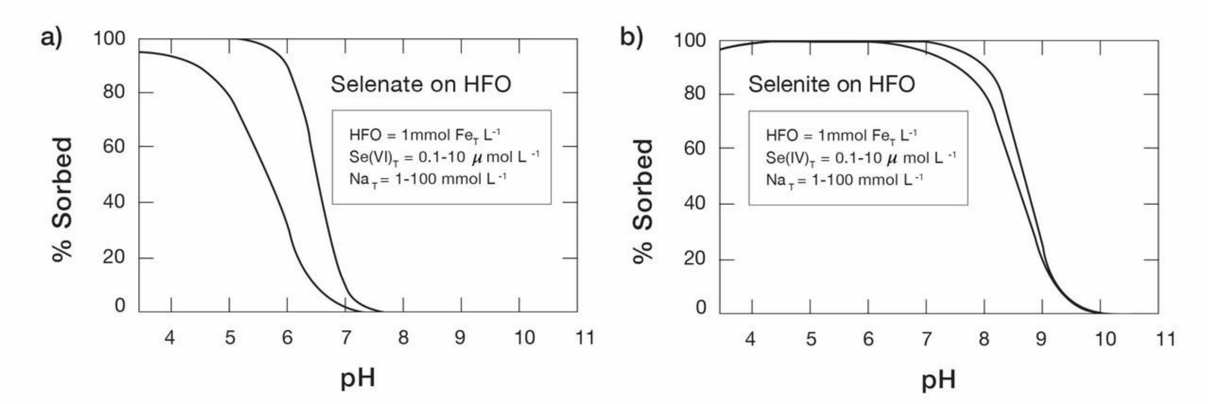

Figure 1.6 a) Calculated Se species adsorbed in an oxidised environment; b) Calculated Se species adsorbed in a reduced environment (Plant et al., 2005).

1.3.4 Mobilisation of As and Se

When trace elements are mobilised, it will be redistributed by complex geochemical processes such as precipitation, water-solid interactions, and colloidal interactions. These processes can be reversible depending on the geochemical environment (Bros et al., 2003; Sami and Druzynski, 2003; Rowland et al., 2011). It is therefore important to understand where these trace elements can potentially be introduced, how they can be sorbed, as well as the processes controlling their mobility. It is too complex to characterise the behaviour of these elements in groundwater since the geochemical environment thereof is in constant flux. Therefore, modelling programs such as PHREEQC and Geochemical Workbench are used to predict the mobility of trace elements in different geochemical environments (Albarede, 1996). The sorption of As and Se onto Fe-, Al- and Mn-oxides and clays are greater at a low pH and the elements can thus be mobilised when the pH is increased. For example, soils in arid environments are normally enriched in Na and Ca, resulting in a higher soil pH. Under these conditions, As and Se would be mobile, and therefore be more available for plant absorption and possibly contribute more to the contamination of water sources.

The mobilisation of As requires only a slight change in the geochemical conditions, initiated by the oxidation of As-bearing sulphide minerals or the release of sorbed As into solution (decreased adsorption from oxide minerals at high pH in oxidising redox conditions). Conversely, Se is mobilised when Se-bearing minerals oxidise rapidly (Bros et al., 2003; Sami and Druzynski, 2003; Rowland et al., 2011).

Chapter 2 Adsorption potential of arsenic and selenium in two soil substrates: A laboratory study

2.1 Introduction

Elevated levels of As (arsenic) and Se (selenium) in geochemical environments, such as groundwater systems, mine tailings and irrigation water, are of major environmental concern (Mukherjee et. al., 2011). The presence of As and Se in geochemical environments can be from both natural or anthropogenic sources (Mandal and Suzuki, 2002). Elevated concentrations of As and Se in the environment can occur from either natural or anthropogenic activities. Groundwater naturally contaminated with hazardous amounts of As (>1000 μg L^{-1}) can be found in Bangladesh, West Bengal, India, Cambodia, Vietnam, and Myanmar. The natural source of these high levels of As originate from the weathering As-bearing iron oxide minerals found in the Himalaya mountains that are then transferred via river systems, deposited and then released to the aquifer, from where the population draws their drinking water (Benner and Fendorf, 2010; Fendorf et al., 2010). In South Africa elevated levels of As and Se originate mostly from anthropogenic activities, such as mining that concentrates these toxic elements into smaller geochemical environments, for instance in mine tailings, thus increasing the threat due to the formation of a pollution point source.

As and Se can naturally be found in some minerals and rocks (Smedley and Kinniburgh, 2002; Sami and Druzynski, 2003). Consumption of even small amounts of As can be extremely toxic, carcinogenic or even fatal to humans as well as animals (Smith et al., 1998; Rahman et al., 2019). For humans, the consumption of as little as 0.6 mg kg^{-1} body weight of As per day can be lethal, while consuming less can be hazardous (Ratnaike, 2003). Although even small amounts of Se consumed are also toxic, the toxicity of Se is more complex, because Se is both a micro-nutrient as well as hazardous, with a small concentration difference between nutrient deficiency and toxicity to humans. This difference between Se deficiency and toxicity, in the human body, is as little as 360 μg of Se per day. Se deficiency is the consumption of <40 μg per day, and Se toxicity is the consumption of >400 μg per day (WHO, 1996). This small difference indicates why the complete understanding of the behaviour of this element in geochemical environments is extremely important. Environmental guideline values (WHO, 1993; 1996) for As and Se in drinking water are <10 μg As L^{-1} water and <10 μg Se L^{-1} water (WHO, 1993; 1996; SANS, 2015). The soil screening value is <5.8 mg As kg^{-1} soil, while no soil screening value is given for Se (Department of Environmental Affairs, 2008). Any waste extract should, therefore, contain <5 mg L^{-1} As and <1 mg L^{-1} Se and the lowest observed effect levels, in the protection of aquatic life, is established at <190 µg L^{-1} for As and <5 µg L^{-1} for Se (Smith and Huyck, 1999).

Using surface complexation models to predict soil chemical systems has been done by multiple researchers (Goldberg, 1992; Goldberg, 1995; Tadanier and Eick, 2002). Chemically, the elements As and Se are classified as metalloids and occur as anionic chemical species in geochemical environments such as soils, groundwater, and mine tailings. Research on anthropogenic contamination and the rehabilitation thereof focuses mainly on metalloid cations such as copper (Cu), mercury (Hg), cadmium (Cd), lead (Pb) and uranium (U). Geochemical modelling of the adsorption of the metalloid anions such as As and Se in geochemical environments is reported by various authors, using MUSIC and CD surface complexation modelling (Hiemstra et al., 1989; Hiemstra and Riemsdijk, 1996; Hiemstra and Riemsdijk, 1999; Hiemstra and Riemsdijk, 2006; Hiemstra and Riemsdijk, 2009; Favorito et al., 2017; Favirito et al., 2018). The behaviour and thermodynamics of these elements in soils are, however, not yet fully understood (Robinson et al., 2011; Rahman et al., 2019). This study will, therefore, use the double layer diffusion surface complexation model to further determine the adsorption potential and thermodynamics of As and Se in prepared substrates. This collected data can then be used to calculate the adsorption isotherms and equilibrium constants, which can serve and as calibration points for geochemical modelling.

The concentrations of As and Se in the soil solution, and therefore their mobility, is determined by the sorption processes of these elements. The sorption of these elements tends to decrease with an increase in pH due to protonation of hydroxides on the surface of the sorbents (Grossl et al., 1997; Peak and Sparks, 2002). Sorption can be defined as the process during which a solute is removed from solution to the solid phase (Jenne, 1998). Adsorption refers to the bonding of a sorbate onto the solid surface of the sorbent. In contrast, absorption is defined as the diffusion and bonding of the sorbate into the crystal structure of the sorbent. In turn, adsorbate (or sorbate) refers to the process through which the solute sorbs onto the solid phase, while adsorbent (or sorbent) refers to the solid phase itself onto which the sorbate sorbs (Jenne, 1998). Full comprehension of the sorption of elements is essential because sorption firstly controls the mobility (transportation) or immobility of contaminants and plant nutrients secondly determine potential waste management strategies, and thirdly informs on geochemical prospecting (Sami and Druzynski, 2003). According to a study by Plant et al. (2005) in a specific geochemical environment, As or Se adsorption are dependent on the pH, Eh conditions, the metal oxides present, and the montmorillonite clay content, showing a strong correlation even although the dependency may vary. In oxidising conditions, arsenate (As^{5+}) or selenate (Se^{6+}) are well adsorbed at a low pH, and will slowly desorb as pH increases.

In both cases, in oxidising conditions, the adsorption of As and Se seems to be pH-dependent (Plant et al., 2005).

Acid mine drainage (AMD) is a common environmental problem within mine (particularly gold and coal) tailings. AMD has high acidity, high salinity, and high metalloid concentrations, mostly associated with Fe-sulphide minerals (Lindsay et al., 2015). Extremely acidic AMD in mine tailings are typically treated with lime ($CaCO_3$) to increase the pH. This seems to solve the problem because the pH of the tailings is neutralised and the metalloid cations are precipitated or immobilised and will thus not leach into groundwater or be taken up by plants. However, at this higher pH values, metalloid anions might be mobilised, are thus prone to leach into the groundwater, and can be taken up by plants as well as be consumed by humans and animals.

Additionally, multiple studies in South Africa propose the use of treated AMD to irrigate agricultural fields (Jovanovic et al., 1998; Annandale et al., 2001; Jovanovic et al., 2001; Annandale et al., 2002; Jovanovic et al., 2003; Annandale et al., 2017). These studies mainly focus on the effect of salinity and the behaviour of metalloid cations in the soils, crops and groundwater, concluding that the risk and opportunity are feasible. However, little to no attention was given to the behaviour of metalloid anions (As and Se) in most of these studies. This is of major concern because the metalloid anions behave differently to the metalloid cations. Therefore, when this treated AMD is used for irrigation the metalloid anions can be mobile and can thus be taken up by crops or leach to groundwater systems and then consumed by humans. As a result, it is imperative to understand the adsorption, fate, and mobility of As and Se, to prevent contamination of groundwater sources and agricultural fields.

2.2 Material and methods

In this study two artificial (soil) substrates were prepared to approximate the Fe-oxide and clay content of soils commonly found in the Witwatersrand and Karoo areas (Rösner et al., 1998; Land Type Survey Staff, 2000). The Witwatersrand area was chosen due to high As and Se concentrations found in the Witwatersrand gold mine tailings (Hansen, 2018). The Karoo area is a large open arid to semi-arid area, in South Africa, that could be used for irrigated agricultural, but due to water scarcity, the potential is limited. Therefore, mine wastewaters could contribute to developing agriculture in that area, if sufficient quantities thereof are available (Annandale et al., 2001; Annandale et al., 2002). A solution containing As or Se was added to each prepared substrate. The pH was adjusted to four different levels. The prepared solutions were incubated, filtered and then analysed for As or Se in the leachate. The difference between the applied and leachate concentration provided the adsorbed concentrations.

2.2.1 Research design

The study was done using two substrates, two contaminants (As and Se) at a single concentration and four pH values. Three replicates of each treatment were conducted to estimate the variability of the results and to improve the accuracy of the estimate. Due to the homogeneity of the samples, three replicates were deemed to be sufficient (Jarman, 2013).

2.2.2 Substrates

Artificially prepared substrates were used to ensure homogeneity of the samples and to simulate the typical topsoil composition of Karoo and Witwatersrand areas, and to ensure that no As or Se contaminants were present.

Land type data was used to determine the average clay and Fe-oxide content of the topsoils in the Karoo and Witwatersrand areas (Rösner et al., 1998; Land Type Survey Staff, 2000). The data indicated that the Karoo soils have an average of 0.86% Fe-oxides and 15.8% clay, and the Witwatersrand soils have an average of 5.71% Fe-oxides and 30.7% clay (Rösner et al., 1998; Land Type Survey Staff, 2000). The Fe-oxide content was determined using dithionite-citrate-bicarbonate extraction (Land Type Survey Staff, 2000) and therefore includes both Fe-oxides and -hydroxides. The Fe-oxide content, therefore, was adjusted to represent all of the Fe-oxides only, by using a molar mass ratio [$\mathrm{Mr}\ \{Fe(OH)_3\} = \frac{\mathrm{Mr}\ (Fe_2O_3)}{\mathrm{Mr}\ (Fe(OH)_3)}$; Equations 2.1 to 2.3]. Inert fine-grained (<150 µm) quartz sand (obtained from Omega Fine Products in Olifantsfontein) was used as matrix mixed with montmorillonite clay (dam sealing bentonite clay obtained from G&W Base and Industrial Minerals (PTY) Ltd) and Fe-hydroxide (goethite obtained from Sigma-Aldrich (PTY) LTD). The mass of goethite, montmorillonite and quartz used in the preparation of the substrates are given in Table 2.1.

$$\mathrm{Mr}[Fe(OH)_3] = \frac{\mathrm{Mr}\ (Fe_2O_3)}{\mathrm{Mr}\ (Fe(OH)_3)} = \frac{159.69}{106.87} = 1.49 \tag{2.1}$$

$$\text{Witwatersrand substrate Fe content} = 1.49 \times 5.71 = 8.53\% \tag{2.2}$$

$$\text{Karoo substrate Fe content} = 1.49 \times 0.86 = 1.29\% \tag{2.3}$$

Table 2.1 Composition of the substrates prepared for this study to replicate that of the Witwatersrand mine tailings and the dominant soils of the Karoo.

Component	Witwatersrand substrate		Karoo substrate	
	(%)	(g)	(%)	(g)
Goethite	8.5	299	1.3	45
Montmorillonite	30.7	1075	15.8	553
Quartz	60.8	2127	82.9	2902
Total	100.0	3500	100.0	3500

2.2.3 Methodology

The batch leach experiment was done by adding 100 g substrate into a 1 L plastic container. Thereafter, 700 mL of a solution containing 1 mg L^{-1} of either As (as arsenate, AsO_4^{-3}) or Se (as selenate, SeO_4^{-2}) was added to each soil substrate sample. These solutions used were made by mixing, for As 7.67 mg As_2O_5 with 5 L deionised water, and for Se 7.03 mg SeO_2 with 5 L deionised water. The As_2O_5 (with a solubility in water of 658 g L^{-1} at 20°C) and O_2Se (with a solubility in water of 400 g L^{-1} at 20°C) were procured from Sigma-Aldrich in South Africa. The amount of As and Se oxides used were calculated, by using the molar mass of the oxides and the elemental ratio, together with the desired concentration ($\frac{\mathrm{Mr}\ [As_2O_5]}{As_2}$ x 1 mg L^{-1}; $\frac{Mr[O_2Se]}{Mr[Se]}$ x 1 mg L^{-1}). These solutions were then analysed to confirm that the specific concentrations of the As and Se in solution are 1 mg L^{-1}. The concentration of 1 mg L^{-1} was chosen to represent a balance between a concentration high enough to observe the adsorption and low enough to replicate concentrations of As and Se typically found in anthropogenically impacted geochemical environments.

The pH of the solution in the containers was then adjusted to 2, 5, 7 or 9 respectively. To do this, the pH was measured and then either reduced by adding hydrochloric acid (HCl, 38%) or increased by adding 1 N sodium hydroxide, until the desired pH value was reached. The substrates were then mixed for 24 hours using orbital stirrer and then left to settle for 24 hours at 25°C, while partially covered and exposed to the atmosphere, thus maintaining an oxidising environment. After 24 hours, the solution was filtered through a 0.2 µm micro-pore filter and the filtrate analysed for As or Se. A 0.2 µm filter was used because particles smaller than 0.2 µm are defined as being in solution (Bruland and Rue, 2001). Analyses were done through the commercial laboratory Waterlab, using an ICP-MS (Inductively Coupled Plasma Mass Spectrometer). Any results that returned <0.001 mg L^{-1} were assumed to be zero, since this was the lower detection limit for As on the ICP-MS, as specified by the instrument's manufacturer. The adsorbed As or Se were then calculated as the As or Se added (1 mg L^{-1}) the minus As or Se determined in the solution. The data thus obtained were then used to calculate the equilibrium constants for the sorption reactions of As and Se respectively.

2.3 Results

2.3.1 Influence of pH on sorption

Analytical results for the As or Se in solution, the calculated As or Se adsorbed by the Fe-oxide and montmorillonite clay in the substrates, and the calculated adsorption percentage are given in Table 2.2 to Table 2.5.

Table 2.2 Analytical results of As in solution and the calculated As sorbed for each pH treatment, in the Witwatersrand substrate.

pH	Sample No.			Mean	Standard error	Adsorption	Adsorption
	1	2	3				
	mg L^{-1}						%
2	0.001	0.000	0.000	0.000	0.0003	1.000	100
5	0.000	0.000	0.000	0.000	0.0000	1.000	100
7	0.001	0.000	0.001	0.000	0.0003	1.000	100
9	0.007	0.006	0.004	0.006	0.0009	0.994	99.4

Table 2.3 Analytical results of Se in solution and the calculated Se sorbed for each pH treatment, in the Witwatersrand substrate.

pH	Sample No.			Mean	Standard error	Adsorption	Adsorption
	1	2	3				
	mg L^{-1}						%
2	0.001	0.001	0.002	0.001	0.0003	0.999	99.9
5	0.003	0.002	0.002	0.002	0.0003	0.998	99.8
7	0.017	0.012	0.018	0.016	0.0019	0.984	98.4
9	0.222	0.168	0.384	0.258	0.0649	0.742	74.2

Table 2.4 Analytical results of As in solution and the calculated As sorbed for each pH treatment, in the Karoo substrate.

pH	Sample No.			Mean	Standard error	Adsorption	Adsorption
	1	2	3				
	mg. L^{-1}						%
2	0.011	0.012	0.013	0.012	0.0006	0.988	98.8
5	0.002	0.003	0.003	0.003	0.0003	0.997	99.7
7	0.027	0.044	0.019	0.030	0.0074	0.970	97.0
9	0.114	0.150	0.056	0.107	0.0274	0.893	89.3

Table 2.5 Analytical results of Se in solution and the calculated Se sorbed for each pH treatment, in the Karoo substrate.

pH	Sample No.			Mean	Standard error	Adsorption	Adsorption
	1	2	3				
	mg. L^{-1}						%
2	0.011	0.009	0.013	0.011	0.0012	0.989	98.9
5	0.046	0.051	0.052	0.0497	0.0019	0.950	95.0
7	0.370	0.246	0.396	0.3373	0.0462	0.663	66.3
9	0.704	0.729	0.688	0.7070	0.0119	0.293	29.3

Adsorption isotherms express the adsorption at a specific pH and at a given pressure and temperature. In this experiment, these were standard conditions, i.e. 25°C and 1 atm. The adsorption isotherms for As and Se in the Witwatersrand and Karoo substrates are given in Figure 2.1 to Figure 2.4.

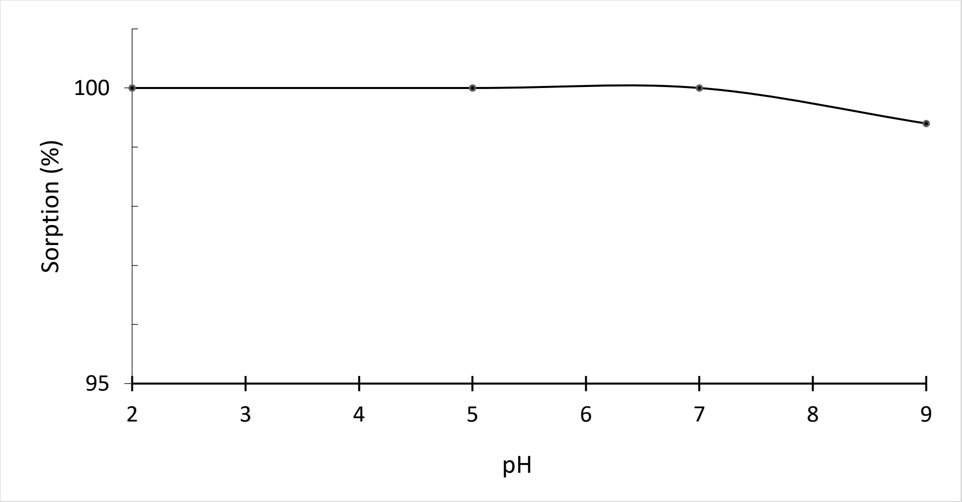

Figure 2.1 Adsorption edge of As (%) for each pH treatment, in the Witwatersrand substrate.

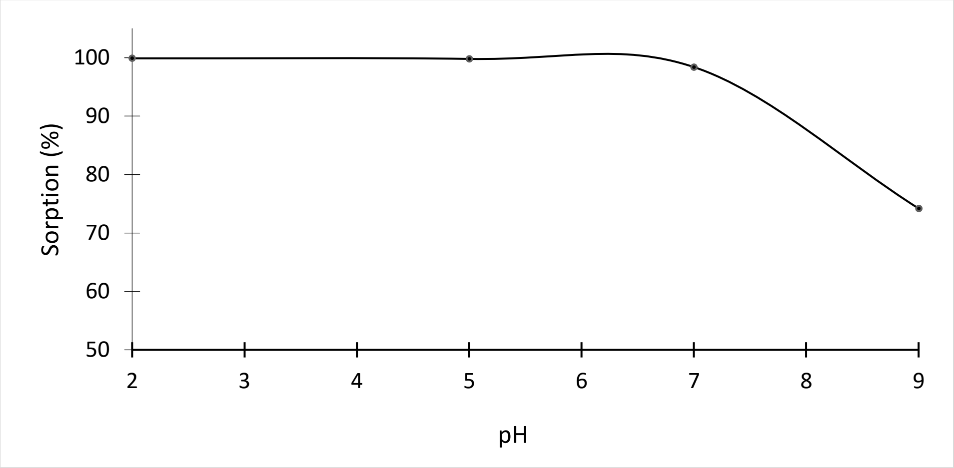

Figure 2.2 Adsorption edge of Se (%) for each pH treatment, in the Witwatersrand substrate.

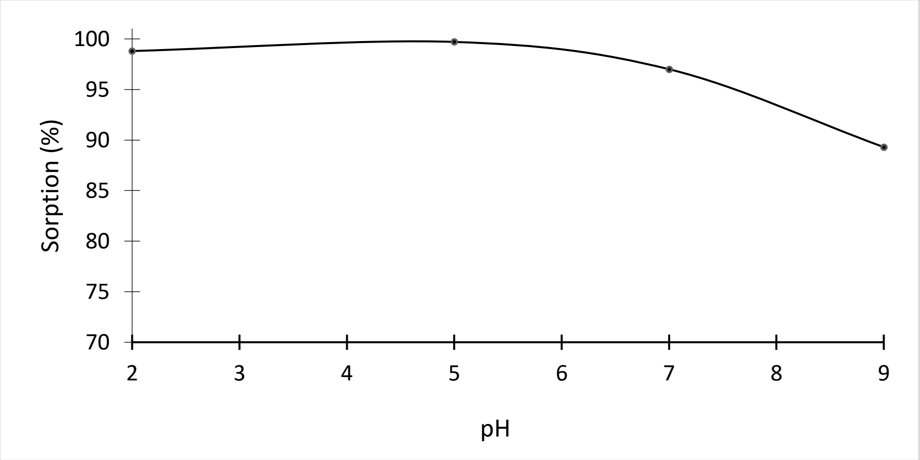

Figure 2.3 Adsorption edge of As (%) for each pH treatment, in the Karoo substrate.

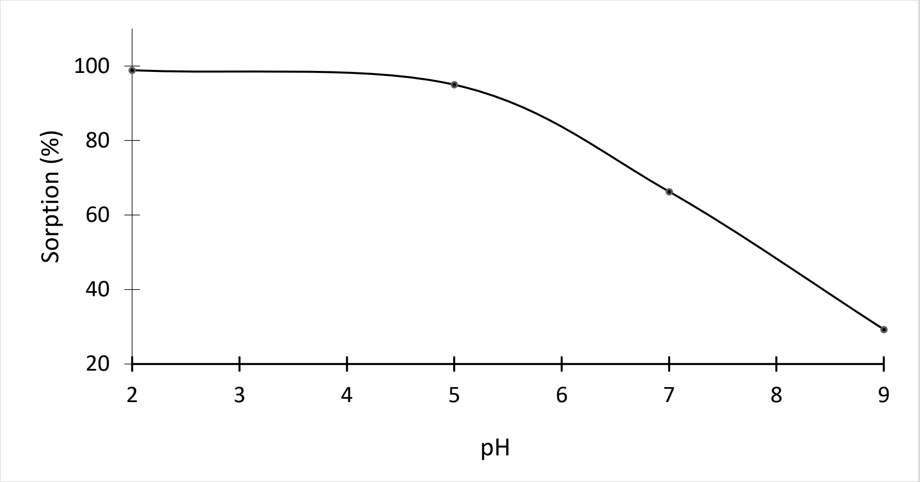

Figure 2.4 Adsorption edge of Se (%) for each pH treatment, in the Karoo substrate.

In these graphs, it was evident that most of the As was sorbed at all pH values, while Se was significantly less sorbed at alkaline pH values, compared to As. Decreased adsorption of As only started at a pH >7, and less than 15% remained in solution; while Se adsorption started to decrease form a pH >5, and up to 80% of the Se remained in solution.

2.4 Discussion

Both As and Se were fully adsorbed at a low pH and this adsorption decreased as the pH increased (Table 2.2 to Table 2.5; Figure 2.1 to Figure 2.4). This corresponded with the expected behaviour of As and Se (Dzombak and Morel, 1990; Bros et al., 2003; Plant et al., 2005; Ahamed et al., 2009; Moreno-Jimenez et al., 2013). In both substrates, As adsorbed stronger and the adsorption only started to decrease slightly at a higher pH (between 7 to 9). The decreased adsorption of Se appeared to occur much faster than that seen with As, starting at a pH >5. This phenomenon was most likely because As is a siderophile and the affinity of As for Fe-oxides is much higher than that of Se (Eby, 2004). This observation was also supported by the difference in sorption of As between the Witwatersrand and Karoo substrates because the Witwatersrand substrate contained almost ten times more Fe-oxides (5.7%) than the Karoo substrate (0.86%). Arsenic was, therefore, stronger adsorbed in the Witwatersrand than in the Karoo substrate and the adsorption of As therefore started to decrease at a higher pH in the Witwatersrand substrate than in the Karoo substrate.

A decrease in the adsorption and therefore an increase in mobility of As and Se in the Witwatersrand substrate only started at an estimated pH >6, whereas the decrease in adsorption started at an estimated pH >5 in the Karoo substrate. This was interpreted to be due to the higher amount of montmorillonite clay and Fe-oxides in the Witwatersrand substrate in relation to the Karoo substrate, providing more adsorption sites.

At a pH of 9, in both substrates 70% or more Se and about 10% of As was not adsorbed, and therefore mobile. This mobile As and Se can either possibly leach into groundwater systems or it can be taken up by plants and can thus be consumed by humans and animals (Bunzl et al., 2001; Cao et al., 2003; Huang et al., 2006; Favorito et al., 2017).

2.5 Equilibrium constants

The equilibrium constants (K_{eq} and log of the equilibrium constant of the reaction, Log_K) were calculated for the sorption data obtained through the experiments. The Log_K, for this specific system, was determined for reactions 2.4, 2.6, 2.8, 2.10 and 2.12 by using equations 2.5, 2.7, 2.9, 2.11 and 2.13 given below. For each reaction, a Log_K was determined for the specific pH (2, 5, 7, and 9 respectively) and a specific substrate (Witwatersrand and Karoo respectively). The release rates of these reactions are almost immediate and were therefore not significant to this study (Peak and Sparks, 2002; Bethke, 2008). These reactions and equations used below were sourced from Dzombak and Morel (1990) and Bethke (2008). The Log_K of these reactions were calculated by using the equations given below and the experimental parameters discussed in section 2.2.3. The concentration H^+ present in the system was calculated by using the formula $[\mathrm{H}^+] = 10^{-(pH)}$ and the concentrations of As (as AsO_4^{3-}) and Se (as SeO_4^{2-}) were taken as 1 mg L^{-1}, since this was the concentration applied to the substrates in this study. The value used for the concentration of water present was taken as 1, this was used for simplicity purposes since the water in the system does not greatly contribute to the K_{eq}. In this study the site densities used in the calculations were obtained by using the composition of the substrates and known data on the site densities of goethite and montmorillonite (Dzombak and Morel, 1990; Villalobos et al., 2003; Tournassat et al., 2018). The site density of the Witwatersrand substrate was thus calculated to be 0.88 mol sites nm^{-2} and 0.36 mol sites nm^{-2} for the Karoo substrate.

$$\mathrm{Hfo\_wOH} + \mathrm{AsO_4^{3-}} + 3\mathrm{H^+} = \mathrm{Hfo\_wH_2AsO_4} + \mathrm{H_2O} \tag{2.4}$$

$$K_{eq} = \frac{[\mathrm{Hfo\_wH_2AsO_4}][\mathrm{H_2O}]}{[\mathrm{Hfo\_wOH}][\mathrm{AsO_4^{3-}}][\mathrm{H^+}]^3} \tag{2.5}$$

where: Hfo_wOH = weak hydrous ferric oxide sorption site, goethite in this study (Bethke, 2008)

K_{eq} = equilibrium constant

Table 2.6 Equilibrium constants of As (as AsO_4^{3-}) for the Witwatersrand and Karoo substrates, at the selected pH values, calculated using equations 2.4 and 2.5.

Substrate	pH	K_{eq}	Log_K
Witwatersrand	2	$1.13x10^{6}$	6.06
	5	$1.14x10^{15}$	15.1
	7	$1.14x10^{21}$	21.1
	9	$1.13x10^{27}$	27.1
Karoo	2	$2.72x10^{6}$	6.44
	5	$2.75x10^{15}$	15.4
	7	$2.67x10^{21}$	21.4
	9	$2.46x10^{27}$	27.4

$$Hfo\_wOH + AsO_4^{3-} + 2H^+ = Hfo\_wHAsO_4^- + H_2O \qquad (2.6)$$

$$K_{eq} = \frac{[Hfo\_wHAs0_4^-][H_2O]}{[Hfo\_wOH][AsO_4^{3-}][H^+]^2} \qquad (2.7)$$

where: Hfo_wOH = weak sorption site, goethite in this study (Bethke, 2008)

K_{eq} = equilibrium constant

Table 2.7 Equilibrium constants of As (as AsO_4^{3-}) for the Witwatersrand and Karoo substrates, at the selected pH values, calculated using equations 2.6 and 2.7.

Substrate	pH	K_{eq}	Log_K
Witwatersrand	2	$1.14x10^{4}$	4.06
	5	$1.14x10^{10}$	10.1
	7	$1.14x10^{14}$	14.1
	9	$1.13x10^{18}$	18.1
Karoo	2	$2.72x10^{4}$	4.44
	5	$2.75x10^{10}$	10.4
	7	$2.67x10^{14}$	14.4
	9	$2.46x10^{18}$	18.4

$$Hfo\_wOH + AsO_4^{3-} + H^+ = Hfo\_wAsO_4^{2-} + H_2O \qquad (2.8)$$

$$K_{eq} = \frac{[Hfo\_wAsO_4^{2-}][H_2O]}{[Hfo\_wOH][AsO_4^{3-}][H^+]} \qquad (2.9)$$

where: Hfo_wOH = weak sorption site, goethite in this study (Bethke, 2008)

K_{eq} = equilibrium constant

Table 2.8 Equilibrium constants of As (as AsO_4^{3-}) for the Witwatersrand and Karoo substrates, at the selected pH values, calculated using equations 2.8 and 2.9.

Substrate	pH	K_{eq}	Log_K
Witwatersrand	2	$1.14x10^{2}$	2.06
	5	$1.14x10^{5}$	5.06
	7	$1.14x10^{7}$	7.06
	9	$1.13x10^{9}$	9.05
Karoo	2	$2.72x10^{2}$	2.44
	5	$2.75x10^{5}$	5.44
	7	$2.67x10^{7}$	7.43
	9	$2.46x10^{9}$	9.39

$$\text{Hfo\_wOH} + SeO_4^{2-} + 2H^+ = \text{Hfo\_wHSeO}_4 + H_2O \qquad (2.10)$$

$$K_{eq} = \frac{[\text{Hfo\_wHSeO}_4][H_2O]}{[\text{Hfo\_wOH}][SeO_4^{2-}][H^+]^2} \qquad (2.11)$$

where: Hfo_wOH = weak sorption site, goethite in this study (Bethke, 2008)

K_{eq} = equilibrium constant

Table 2.9 Equilibrium constants of Se (as SeO_4^{2-}) for the Witwatersrand and Karoo substrates, at the selected pH values, calculated using equations 2.10 and 2.11.

Substrate	pH	K_{eq}	Log_K
Witwatersrand	2	$1.13x10^{7}$	4.06
	5	$1.13x10^{7}$	10.1
	7	$1.12x10^{7}$	14.0
	9	$8.42x10^{17}$	17.9
Karoo	2	$2.72x10^{7}$	4.44
	5	$2.62x10^{7}$	10.4
	7	$1.83x10^{14}$	14.3
	9	$8.07x10^{17}$	17.9

$$\text{Hfo\_wOH} + SeO_4^{2-} + H^+ = \text{Hfo\_wSeO}_4^- + H_2O \qquad (2.12)$$

$$K_{eq} = \frac{[\text{Hfo\_wSeO}_4^{2-}][H_2O]}{[\text{Hfo\_wOH}][SeO_4^{2-}][H^+]} \qquad (2.13)$$

where: Hfo_wOH = weak sorption site, goethite in this study (Bethke, 2008)

K_{eq} = equilibrium constant

Table 2.10 Equilibrium constants of Se (as SeO_4^{2-}) for the Witwatersrand and Karoo substrates, at the selected pH values, calculated using equations 2.12 and 2.13.

Substrate	pH	K_{eq}	Log_K
Witwatersrand	2	$1.12x10^{2}$	2.05
	5	$1.13x10^{5}$	5.05
	7	$1.12x10^{7}$	7.05
	9	$8.42x10^{8}$	8.93
Karoo	2	$2.72x10^{2}$	2.44
	5	$2.62x10^{5}$	5.42
	7	$1.83x10^{7}$	7.26
	9	$8.07x10^{8}$	8.91

The calculated equilibrium constants (K_{eq}) and log of the equilibrium constants (Log_K) for the known and expected species of As and Se in the experiments are given in Tables 2.6 to 2.10. The species of As and Se used in these reactions are the species of As and Se that are defined by Dzombak and Morel (1990), and that were also used in the geochemical modelling program PHREEQC. The speciation of As and Se were modelled in PHREEQC and are discussed in the next chapter. When referring to hydrous ferric oxides here, it should be assumed that the goethite used in this study was used as is the hydrous ferric oxide proxy.

The Log_K values calculated in this study differed from the calculated Log_K in published literature, since the specified conditions differed. The surface species and log of the equilibrium constant of the reaction (Log_K) of the arsenate and selenate reactions, as defined by Dzombak and Morel (1990) is given in equations 2.14 to 2.18 below.

$Hfo\_wOH + AsO_4^{3-} + 3H^+ = Hfo\_wH_2AsO_4 + H_2O$ Log_K 31.00 (2.14)

$Hfo\_wOH + AsO_4^{3-} + 2H^+ = Hfo\_wHAsO_4^- + H_2O$ Log_K 26.81 (2.15)

$Hfo\_wOH + AsO_4^{3-} + H^+ = Hfo\_wAsO_4^{2-} + H_2O$ Log_K 20.22 (2.16)

$Hfo\_wOH + SeO_4^{2-} + 2H^+ = Hfo\_wHSeO_4 + H_2O$ Log_K 16.6 (2.17)

$Hfo\_wOH + SeO_4^{2-} + H^+ = Hfo\_wSeO_4^- + H_2O$ Log_K 22.3 (2.18)

By comparing the Log_K values calculated for this study against those defined by Dzombak and Morel, 1990, it is evident that the Log_K values calculated in this study are lower than the values defined by Dzombak and Morel, 1990. It cannot be assumed that all the Log_K values will all apply to the specific goethite and montmorillonite clay used in this study. The lower Log_K is most likely due to the difference in site densities in the two studies. In this study the site densities determined were, as closely represented as possible, to the amount of both the Fe-oxides and montmorillonite clay present in this study. Whereas in the study of Dzombak and Morel (1990) the site densities used were only those of Fe-oxides.

The only other moderately comparable published Log_K values are those presented in reactions 2.19 to 2.22 below. These reactions give the Log_K values of arsenate and selenate reactions published by Bothe (1999) and Wu et al. (2000).

$AsO_4^{3-} + H^+ = HAsO_4^{2-}$ Log_K 11.60 (2.19)

$HAsO_4^{2-} + H^+ = H_2AsO_4^-$ Log_K 6.76 (2.20)

$HSeO_4^{2-} = H^+ + SeO_4^{2-}$ Log_K 1.92 (2.21)

$SOH + H^+ + SeO_4^{2-} = SOH_2^+ - SeO_4^{2-}$ Log_K 9.8 (2.22)

Interrogation of the calculated Log_K values of these reactions clearly indicates that the scenarios, parameters, and the reactions are too different to compare the Log_K values thereof with those obtained in this study.

The study by Dzombak and Morel (1990) can be regarded as the first detailed definition of surface complexation modelling on hydrous ferric oxide. In their study, they describe the Log_K of numerous species of elements including the species of As and Se. There are many studies defining the Log_K of similar reactions, but it cannot be assumed that all the Log_K values will apply to the specific goethite and montmorillonite minerals and there specific ratios, used in this study (Balistrieri and Chao, 1987; Dzombak and Morel, 1990; Peak and Sparks, 2002).

In this study, the Log_K for the same species at different pH values differed, which should not be the case. This could be due to the fact that the concentration of H^+ ions will vary in accordance with the different pH values, resulting in different Log_K values. However, this observation might also be due to the fact that the speciation of both As and Se are not yet well understood or defined. The species used above and that was defined by Dzombak and Morel (1990), including H_2AsO_4, $HAsO_4^-$, AsO_4^{2-}, $HSeO_4$, and SeO_4^-, do also not include or represent all the possible species of As and Se that can form within a specific environment. However, this does not negate the value of the calculated Log_K values, because the calculated Log_K values encompass all possible species, even though all of these species were possibly not known or defined. More possible species can thus form, which are not yet determined. This aspect is thus recommended for further study.

2.6 Conclusions

This laboratory study on the sorption of As and Se in two artificially created substrates has shown that As and Se adsorption decreases with an increase in pH, as was expected from literature. The mobility of both As and Se in oxidising conditions is, therefore, pH-dependent and their mobility will increase with an increase in pH. It was also apparent that Se was less strongly adsorbed and will, therefore, have a higher mobility than As. This was probably due to As that has a higher affinity for Fe-oxides than Se does. Due to this affinity, As will start to adsorb less only at a higher pH (with the decrease in adsorption starting at a pH >7 in the Witwatersrand substrate and a pH >5 in the Karoo substrate) than Se (with decreased adsorption starting at a pH >6 in the Witwatersrand substrate and a pH >4 in the Karoo substrate). The decreased adsorption of Se, therefore, started about one pH unit lower than As in both the Witwatersrand and the Karoo substrates. Furthermore, the calculated log of equilibrium constants (Log_K) made it evident that the surface complexation and the speciation within these systems were much more complex than that was expected. The speciation of As and Se, under these conditions and the Log_K of each species, are thus not yet fully understood. Therefore, it is highly recommended to further study the speciation of these elements within these conditions. Additionally, it was determined that the Log_K of a reaction is highly dependent on the parameters and conditions of certain reactions. These parameters and conditions, with the largest influence on Log_K, include the specific species present, the site densities of the sorbent, and the pH. Another important outcome of this study was that the experimental data obtained could be used as calibration points for geochemical modelling, to further elucidate the behaviour of As and Se in these environments.

Finally, it was concluded that at the highest pH of 9, no more than 15% of the added As not adsorbed in both the artificially prepared Witwatersrand and Karoo substrates and that pollution of As would, therefore, within the parameters stated for this study, not be of major environmental concern in the Witwatersrand and Karoo substrates at a pH <9. However, between 30% and 70% of Se was not adsorbed in both the Witwatersrand and the Karoo substrates between a pH of 5 and 9. Thus, within the parameters of this study, the decreased adsorption of Se should of environmental concern and Se might thus be likely to leach into groundwater systems or it can be taken up by plants and thus enter into the food chain. Irrigation with Se containing wastewater should therefore not be recommended in these environments.

Chapter 3 Adsorption potential of arsenic and selenium in different soil substrates: A geochemical modelling study

3.1 Introduction

Significant increases in anthropogenic activities over the last few decades highlighted the hazardous effects of industrialisation and mining. Research, awareness, and conversation on the environmental impacts of anthropogenic activities are at an all-time high, and therefore studies about these environmental impacts and the rehabilitation of the impacted areas (*e.g. mine tailings and the waste they produce*) have increased (Nordstrom and Alpers, 1999; Nordstrom, 2012; Hansen, 2018; Rahman et al., 2019). Numerous studies have been done on the sorption potentials of metalloid cations in mine tailings and soils. However, less attention has been given to the sorption potential of the metalloid anions, specifically focussing on mine and industrially impacted soils in the "natural" environment.

These aspects recently became the focus of society due to the magnitude of the deleterious environmental impacts, especially in the rehabilitation of mine tailings and mine-affected waters not only in South Africa but globally, for three main reasons. Firstly, the behaviour of most metalloid anions is not well understood. Secondly, environmental consultants who mostly conduct the pre-mining environmental impact assessments, do not pay enough attention to the probability of metalloid anions leaching out of mine tailings in high pH conditions in the long term. Thirdly, the increase and presumed success of irrigating agricultural fields with mine-affected waters (Annandale et al., 2002; Annandale et al., 2017; Grewar, 2019).

Acid mine drainage (AMD) refers to mine wastewater, with high acidity, relatively high salinity, high metalloid concentration, and is mostly associated with Fe-sulphide minerals (Lindsay et al., 2015). AMD is a well-known problem associated with mine tailings, especially in gold and coal mines. This leads to extremely acidic mine wastewater, often concentrated in tailings, which are mostly treated with lime to increase the pH. After this treatment, the metalloids cations are stable and immobilised, with most environmentalists then satisfied. But in that environment, i.e. under approximately neural to alkaline pH values, metalloid anions are potentially mobilised and thus prone to leaching to the groundwater or soil or substrate, and can be taken up by plants and thus be consumption by humans and animals.

The neutralised AMD has been used in multiple studies (Jovanovic et al., 1998; Annandale et al., 2001; Jovanovic et al., 2001; Annandale et al., 2002; Jovanovic et al., 2003; Annandale et al., 2017) as irrigation water for agriculture. These studies mainly focus on the effect and behaviour of salinity and the metalloid cations in the soils, crops and groundwater, thus pointing to feasible risk and opportunity assessments (Annandale et al., 2002; Annandale et al., 2017). But in most of these studies, little to no attention was given to the geochemical behaviour of metalloid anions.

Arsenic (As) and selenium (Se) are two metalloid anions amongst other metalloids such as uranium (U), molybdenum (Mo), silver (Ag), vanadium (V), tin (Sn) and chromium (Cr). This study will focus on As and Se because these elements are mobile under a larger range of naturally occurring groundwater conditions, having a higher hazard rating than many other trace constituents (Sami and Druzynski, 2003) and also because these elements are commonly found in gold mine tailings and the surrounding environments. Due to the geochemical similarities of As and Se, it is assumed that their geochemical behaviour will be similar. As and Se, unlike other metalloids, can be mobilised relatively easily under a range of different pH and Eh conditions which will conceivably contribute to greater environmental contamination. Both As and Se can be hazardous and toxic to humans when consumed in trace amounts and therefore becomes a risk for possible consumption (WHO, 1993; 1996).

Internationally, the naturally occurring metalloid anions As and Se were not listed as contaminants in drinking water or routinely analysed until fairly recently, because little is known about their distribution. Subsequently impacted areas, exceeding guidelines, were only recognised after serious effects were seen on human and animal health (Sami and Druzynski, 2003). Large quantities of both As and Se can be hazardous or even fatal. A consumption amount of 0.6 mg kg^{-1} body weight As per day can be lethal to humans (Ratnaike, 2003). Se toxicity is more complicated than As since Se is a micronutrient. Se deficiency (<40 µg day^{-1}) and toxicity (>400 µg day^{-1}) can be hazardous or even fatal to human health (WHO, 1996). The small range between Se deficiency and toxicity indicates the importance of understanding the behaviour of Se. Furthermore, the guideline value for As in drinking water is <10 µg L^{-1} (WHO, 1993; SANS, 2015) and the soil screening value (SSV) of the amount of As that can be present in a soil protective of human health and water resources (SSV 1) is <5.8 mg kg^{-1} (Department of Environmental Affairs, 2008). In South Africa, according to the South African National Standard, the drinking water guideline for Se is <40 mg L^{-1} (SANS, 2015). Even though the WHO guideline for Se in drinking water is <0.01 mg L^{-1} (WHO, 1996) and no SSV of Se could be found (Department of Environmental Affairs, 2008). The knowledge gained in this study can be crucial in the remediation and rehabilitation of metalloid contaminated water worldwide. Although some guidelines are now available, the long-term pedo-geochemical processes present in environmental systems were not taken into account. Geochemical modelling is therefore extremely important to understand these processes.

Sorption describes the removal of a solute (element or compound) from solution to the solid phase. Adsorption refers to the precipitation of a sorbate on a sorbent surface, while absorption refers to the diffusion and precipitation of a sorbate into the crystal structure of the sorbent. The term adsorbate (or sorbate) thus refers to the action of solute transfer to the solid phase surface, while adsorbent (or sorbent) refers to the solid phase surface onto which the sorbate sorbs (Jenne, 1998).

The adsorption of As or Se, in a specific geochemical environment, is almost totally affected by the prevalent pH and Eh conditions, as well as the metal oxides and montmorillonite clay present. The metal oxides and montmorillonite clay minerals act as sorbents and thus provide the sorption sites for the sorbates. The effects of Eh (redox potential) and pH on the adsorption of As and Se are discussed by Plant et al. (2005). They concluded that in oxidising conditions, arsenate (As^{5+} as $H_2AsO_4^-$) and/or selenate (Se^{6+} as SeO_4^{-2} or O_4Se_2) strongly adsorb on Fe-oxides and montmorillonite clays at a lower pH and slowly desorbed as the pH increased. This is most likely due to repulsion between the negatively charged sorbate surface and As or Se anion. On the contrary, in reducing conditions as arsenite (As^{3+} as AsO_4^{3-}) and/or selenite (Se^{4+} as SeO_3^{2-} or O_3Se^{-2}) tend to be more strongly adsorbed over a wider pH range and sorption thereof thus seems to be almost pH-independent (Plant et al., 2005).

Geochemical modelling uses thermodynamic and chemical equilibria to account for geochemical processes (Bethke, 2008; Hansen, 2018). Geochemical modelling has been used in remediation, risk assessments, mineral and hazardous waste characterisation, environmental consultation, and aqueous geochemistry (Zhu and Anderson 2002; Bethke, 2008). One complicating factor in the use of geochemical modelling for adsorption behaviour is due to the general absence of long-term monitoring data, especially for soils and substrates, which reduce confidence in the geochemical modelling results (Hansen, 2018).

Model confidence building is discussed by Oreskes et al. (1994), Bredehoeft (2005) and Nordstorm (2012). They contend that models are not flawless and definitely not perfect. Models thus only give an approximation and do not provide an exact answer and can never substitute reliable and relevant field data. They also emphasise that instead of proving a model to be correct and attempting to validate it, confidence should rather be built around and in the model. Model confidence can be built in multiple ways, with the most common and effective way by comparing model results with independent observations. Conceptual and numeric models are powerful tools in understanding the processes in a geochemical system and the effects thereof. The objective is thus not to recreate reality, but to develop a model that is accurate enough to be used for the understanding and long-term evaluation of geochemical materials and processes in specific geochemical environments. Therefore, experimental data is a useful means to determine whether a model at least approximates the suspected geochemical processes.

To determine the probability of toxic elements potentially contaminating water sources, a few factors should be considered (Bethke, 2008):

- What is the fate of a toxic chemical in water sources downstream of the contamination source (mine tailings or industrial pollution sites)?
- In what timeframe will the contaminant migrate to a possible contaminated site?
- What processes and reactions will delay or immobilise the contaminant migration?
- What is the environmental impact or what will the toxicity of the contaminant be when concentrations above the regulation thresholds are reached?
- What will the best remediation method include, if remediation is necessary?

Taking all these factors into consideration seemed impossible until geochemical modelling made this possible, creating a “real-life” scenario of possible environmental issues. Geochemical modelling is a relatively new field, and it is extremely important in the environmental assessment field. Geochemical modelling is used to address diverse environmental problems and issues such as mine tailings and mining waste assessment, acid mine drainage, nuclear waste disposal, landfill leachate, bioavailability and risk assessment, chemical weathering and determining and building groundwater flow and solute transportation models (Zhu and Anderson, 2002). With geochemical modelling, two main inadequacies should be noted: Firstly, in geochemical modelling equilibrium is assumed; while numerous surficial processes are not in equilibrium and kinetics rather than equilibrium thermodynamics should be used in modelling. Secondly, the importance of adsorption of solutes onto mineral surfaces should be well established (Bethke, 2008).

Surface complexation modelling, specifically the double layer diffusion model, was used in this study. Although not perfect, this type of modelling was used because it considers the complex configurations and modifications of different parameters to better comprehend the separate planes of the sorbates and their surface charge (Dzombak and Morel, 1990). This type of surface complexation modelling is built on the same fundamentals as that of geochemical modelling. These fundamentals remain the same, including that sorption on oxides take place at coordinated sites and can be quantitatively described by mass laws, the sorption reactions result in the surface charges and the effects of these charges are taking into account by a correction factor (Dzombak and Morel, 1990).

This study formed part of an experimental and geochemical modelling study, which focussed on substrates that have been created to simulate topsoils in the Witwatersrand goldfields as well as in the Karoo. The Witwatersrand and Karoo areas were chosen because the Witwatersrand represents one of the largest mining-impacted regions in South Africa and the Karoo, because it represents almost half the surface area of South Africa and is important for livestock and some crop production. This article is one of two in the overall study. The first article focusses on the experimental procedures and results used for the eventual calibration of the model, while the second article focusses on the geochemical modelling of adsorption behaviour of As and Se. This paper aims to model the geochemical behaviour and adsorption potential of the As and Se metalloid anions on substrates replicating the soils typically found in the mine tailings of the Witwatersrand goldfields and in the Karoo areas.

3.2 Material and methods

The numeric geochemical models were developed by using the USGS geochemical modelling software program, PHREEQC, developed by Parkhurst and Appelo (2013). The numerical model consists of gas, liquid, and solid phase parameters to develop the desired geochemical environment. The database used for this modelling is known as the Lawrence Livermore National Laboratory (LLNL) thermodynamic database (Bethke, 2008). This database is used for the geochemical modelling of systems at earth surface conditions because it is the largest internationally consistent database (Parkhurst and Appelo, 2013). Even though the LLNL database is the largest internationally consistent database for geochemical modelling of systems at Earth surface conditions (Parkhurst and Appelo, 2013) a few modifications were made.

Geochemical models were constructed by firstly developing a conceptual model and then a numeric model. These are discussed in detail below. Surface complexation modelling was done by using the Dzombak and Morel model (Dzombak and Morel, 1990).

3.2.1 Modification of the LLNL database

The LLNL database does not fully describe the surface species of arsenate and selenate, given in the equations below, and therefore does not describe the behaviour As and Se adequately. Surface species added to the database included three species of arsenate (AsO_4^{3-}) and two species of selenate (SeO_4^{2-}). The surface species and log of the equilibrium constant of the reaction (Log_K) of the arsenate and selenate were added (Dzombak and Morel, 1990). For arsenate equation (3.1), (3.2) and (3.3) and selenate equation (3.4) and (3.5) were added to the surface species in the LLNL database (Dzombak and Morel, 1990). Hfo_w represents weak sorption sites. No published specification could be found for the strong sorption sites (Hfo_s) for As and Se.

$Hfo\_wOH + AsO_4^{3-} + 3H^+ = Hfo\_wH_2AsO_4 + H_2O$ Log_K 31.00 (3.1)

$Hfo\_wOH + AsO_4^{3-} + 2H^+ = Hfo\_wHAsO_4^- + H_2O$ Log_K 26.81 (3.2)

$Hfo\_wOH + AsO_4^{3-} + H^+ = Hfo\_wAsO_4^{2-} + H_2O$ Log_K 20.22 (3.3)

$Hfo\_wOH + SeO_4^{2-} + 2H^+ = Hfo\_wHSeO_4 + H_2O$ Log_K 16.6 (3.4)

$Hfo\_wOH + SeO_4^{2-} + H^+ = Hfo\_wSeO_4^- + H_2O$ Log_K 22.3 (3.5)

The geochemical modelling is designed to approximate “real-life” environmental systems and scenarios. In short, these programs build models of natural conditions or environments, which include factors such as temporal, thermodynamic, kinetic, mobilisation of elements and the immobilisation thereof. It also includes the interactions between different chemical phases and components such as solid phase minerals, solutions and other interactive components and as a result simulates specific specified components of a scenario “approximating reality as closely as possible” and of all possible specified interactions in this “real life” time frame. Whenever an environmental issue about contaminants (such as toxic metals or metalloids) arises, the biggest concern is the potential contamination of groundwater and other water sources that might potentially be consumed by humans or by plants and animals, which in turn might be consumed by humans at a later stage (Zhu and Anderson, 2002). In this study, to obtain isolated data on specific variables, a real-life scenario was not replicated but rather the experiments done in the previous chapter. This was done to study the adsorption or behaviour of As and Se in isolation and in doing so to improve the prediction of the behaviour of As and Se in different geochemical environments. This geochemical modelling was done to predict the mobility of As and Se to predict the possible contamination rates of these elements in geochemical systems. This is imperative to predict the potential contamination or even pollution over time and can thus also be used to contribute to the planning and selection of rehabilitation techniques.

For the rehabilitation of contaminated water sources, such as mine tailings and agricultural waste, soil can be a medium which contains constituents (such as montmorillonite clay minerals and Fe-oxides) that have the potential to adsorb elements and can thus ultimately determine whether a specific pollutant will reach groundwater sources of other potential contamination sites.

3.3 Conceptual model

A graphical interpretation of the conceptual model is given in Figure 3.1. This diagram provides a visual explanation of the path through which mine wastewater flows (in the mine tailing and if mine wastewater will be used in irrigation) before reaching the groundwater.

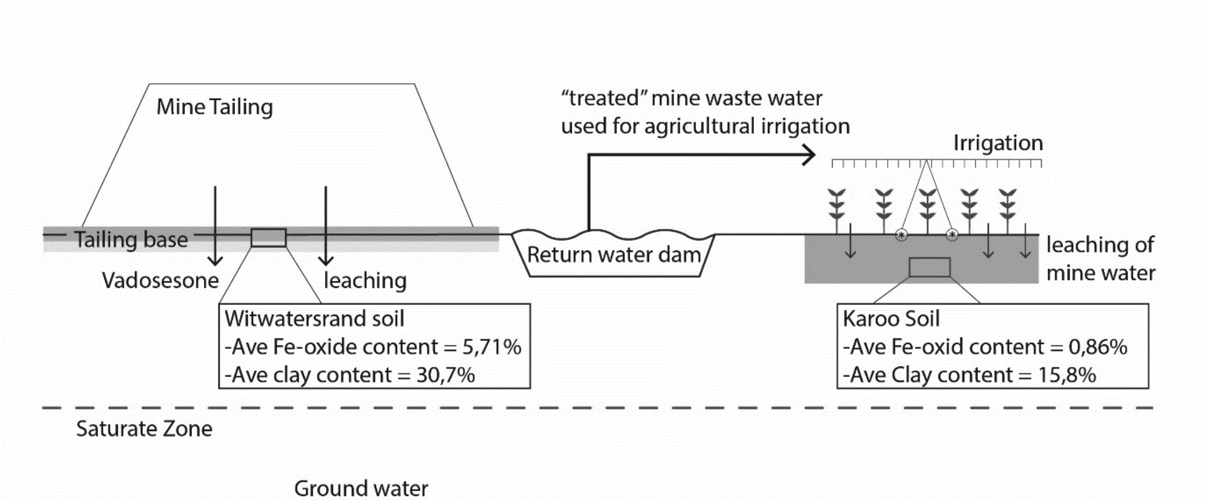

Figure 3.1 Conceptual model of the fate of mine wastewater leaching to underling soils and the fate of treated mine wastewater used for irrigation.

No scientific model can be verified or validated (Oreckes et al., 1994; Nordstorm, 2012). Nevertheless, models are one of the best tools used to aid in understanding and describe geochemical processes in specific systems such as groundwater and mine tailings. In other words, a conceptual model is an idea developed by the researcher(s) based on past experiences. The motive behind the modelling, in this study, is to be able to approximate environmental conditions and processes observed in mine tailings, contaminated soils (from either mine wastewater leaching, mine wastewater irrigation or other anthropogenic activities) and groundwater systems, to model and observe the typical (or most likely) thermodynamic behaviour (until the reactions are in equilibrium with these conditions) of an element within these conditions.

Acid mine drainage (AMD) is one of the most serious environmental impacts and concerns in the mining industry. Acid mine drainage is defined as liquid mine waste solutions with high acidity and relatively high salinity and metalloid concentration, mostly associated with Fe-sulphide minerals (Lindsay et al., 2015). Sulphide minerals are unstable in the presence of strong oxidants, such as the O_2 in the Earth's atmosphere. When Fe-sulphides come into contact with the Earth's atmosphere the sulphide minerals oxidise and release metalloids, SO_4^{-2} and acidity in the form of H^+, that decreases the pH and results in very acidic metalloid rich mine tailings (Nordstrom and Alpers, 1999; Lindsay et al., 2015; Hansen, 2018). These sulphide minerals can contain inclusions of trace metalloids. Therefore, when these minerals oxidise metalloids such as As and Se are released in the mine tailings solutions, which either leaches to the underlying soils and groundwater systems or is pumped into storage dams where the "rehabilitated" mine-affected waters are used as irrigation water for agriculture, thus potentially contaminating the soil and the crops intended for human consumption. Many models describing adsorption is available. Anion adsorption at the solid solution interface of hydroxides plays an important role in environmental chemistry (Hiemstra and Van Riemsdijk, 1996). According to Rietra et. al. (1999), pH dependency is an important characteristic of the macroscopic proton-ion adsorption stoichiometry. In this study, the proton-ion adsorption stoichiometry was determined to successfully predict the spectroscopically identified structures of selenite and arsenate on goethite.

Reactions 3.1 to 3.5 describe the adsorption reactions of arsenate and selenate in an oxidising environment, defined by Dzombak and Morel (1990). In equations 3.1 to 3.5, the adsorption reactions of arsenate (AsO_4^{3-}) and selenate (SeO_4^{2-}) are described. The geochemical modelling was used to study the behaviour of As and Se, and was then calibrated, especially by using the equilibrium constants, with data gained from laboratory experiments given in Chapter 2.

In this study the double layer diffusion model by Dzombak and Morel were used rather than the CD-MUSIC model defined by Hiemstra and van Riemsdijk, 1996. In these reactions, Hfo_wOH represents the weak adsorption or binding sites of the sorbent species. In the case of this study, the sorbent sites were provided by the Fe-oxides and the montmorillonite clay minerals. These sorbent sites were described by Hfo_w for weak sites (and Hfo_s for strong sites) with a hydroxide (OH^-) adsorbed onto the sorbent. In these reactions, hydroxide ions, adsorbed to weak adsorption sites, will exchange with arsenate or selenate respectively. This signifies that, in an oxidising environment, where arsenate or selenate is present the following will happen: The OH^- will dissociate from the crystal structure and will bind with H^+ to form H_2O. This will release the binding site, which can then be occupied by arsenate or selenate. The species of arsenate or selenate adsorbed will vary depending on the amount of H^+ ions present. This includes the species H_2AsO_4, $HAsO_4^-$ and AsO_4^{2-} for arsenate, and $HSeO_4$ and SeO_4^- for selenate, from highest H^+ to lowest H^+ concentration (Dzombak and Morel, 1990). This will all happen in the inner or Stern layer (Hiemstra and Van Riemsdijk, 1996) of the diffuse double layer.

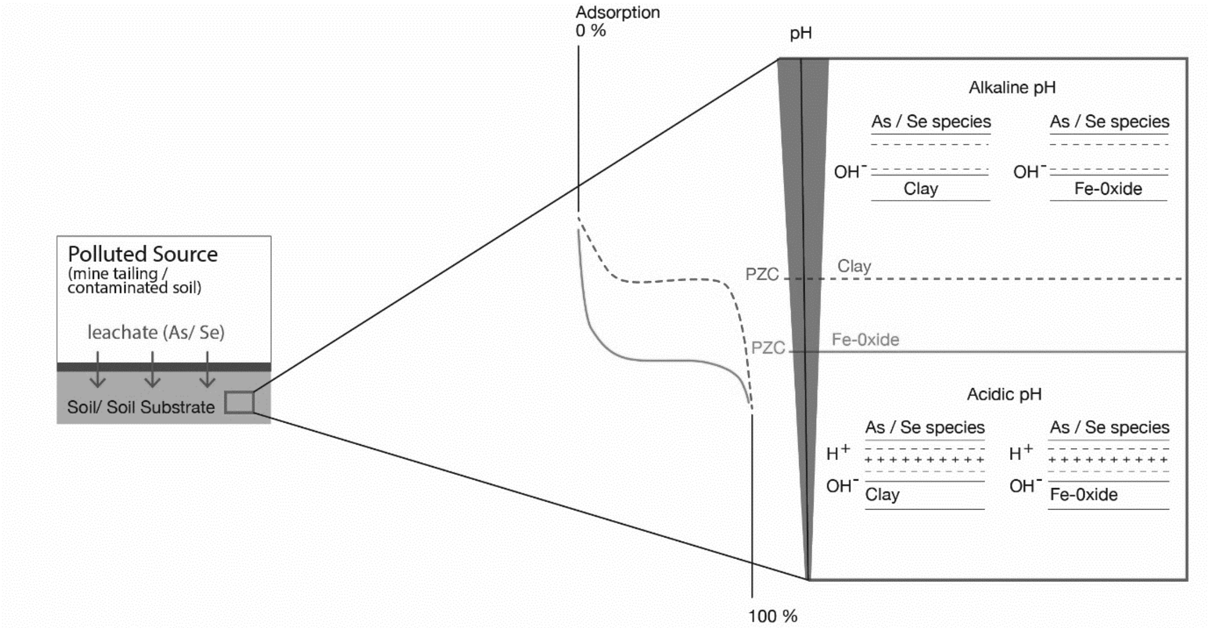

Figure 3.2 A schematic diagram of the adsorption of As or Se by montmorillonite clay or Fe-oxides, through surface charges, in relation to pH.

Equations 3.1 to 3.5 above indicate that the adsorption is dependent on the availability of H^+ in the soils and consequently on the pH. Thus, the adsorption of these elements should be higher at a lower pH, where more H^+ ions are available and the OH^- ions are adsorbed to the adsorption sites (Figure 3.2).

3.4 Numeric model

According to Nordstrom (2012), the numerical model is the mathematical expression and parameterisation of the conceptual understanding of the system or process being studied (conceptual model). In the numeric model, the PHREEQC software program was used to build on the conceptual model by using mathematical expressions and thermodynamics. The numerical model was used to determine the adsorption potential and behaviour of As and Se, respectively, in the defined geochemical environment.

3.4.1 Model setup

To develop a numeric geochemical model in PHREEQC, three crucial input sections were completed. These main inputs include solid phases, a gas phase and a liquid phase.

The solid phase properties are determined by the composition and mineralogy of the substrates. Thus, the solid phases consist of the average percentage of Fe-oxide and montmorillonite clay content and type typically found in Witwatersrand and Karoo soils. To create a substrate consisting of 100% minerals, quartz was added to the Fe-oxides and montmorillonite clay. Quartz was used to fill up the substrates because of its inert properties, i.e quartz is rather inactive and would not interfere with the adsorption of the montmorillonite clay and Fe-oxides. These minerals are presented as pure thermodynamic solid phases and discussed in detail, in section 3.4.2 under development and parameterisation. The liquid phase was entered as solutions with specific pH and Eh conditions. These solutions were entered as distilled water, in an oxidising environment, contaminated with 1 ppm As or Se respectively. More specific details are discussed in section 3.4.2. The gas phase input was entered by replicating the atmospheric conditions of Earth. This included the partial pressure of nitrogen (0.78) and oxygen (0.21) as in the Earth's atmosphere. This is also further discussed in section 3.4.2. Models were then developed for As and Se individually. For each of these elements, different models were developed replicating the different concentrations of the element and different pH values. To gain confidence in these models and consequently this study, the models aimed to replicate the laboratory experiments. The modelled laboratory system was calibrated using the laboratory experiments presented in Chapter 2. The modelling was done by excluding other cation and anion associations to determine the impact of the adsorbents individually.

3.4.2 Development and parameterisation

The geochemical model was developed by replicating a specific concentration of As or Se, in an oxidising environment, in a soil substrate with a defined Fe-oxide and clay mineral content, which is discussed later in the section. This was required to calculate the adsorption of As and Se at certain pH values. The specific details are discussed below.

3.4.2.1 First tier model development and parameterisation

a. Gas phase

The gas phase input into the PHREEQC model, represented the Earth's atmosphere. The Earth's atmosphere is seen as an oxidising environment because of the amount of oxygen freely available. The Earth's atmosphere consists of 21% O_2 and 79% N_2. Thus, the gas phase entered into the PHREEQC model consists of f_{O2} (oxygen fugacity) equal to 0.21 and f_{N2} (nitrogen fugacity) equal to 0.79 therefore together giving a partial pressure of 1 atm. The temperature was kept as default at 25°C.

b. Liquid phase

The liquid phase of this model is very important because the concentration of As or Se and the pH are defined in this phase. Initially the liquid phase consisted of deionized water contaminated with a certain concentration of As or Se respectively, at different pH values. The water mass was entered as 0.7 L at a temperature of 25°C. The water mass of 0.7 L was used to exactly replicate and stay in line with, the water mass used in experimental data (that was used as calibration points; Chapter 2). For each concentration of As or Se, the pH was adjusted to 2, 5, 7 and 9 respectively. Individual element inputs were entered into the model to introduce As or Se to the system. For As^{5+} the species $H_2AsO_4^-$, and for Se^{6+} the species SeO_4^{2-} were entered. Hydrogen was, therefore, the balancing cation. A model was made for each of the elements, As or Se, at a concentration 1 mg L^{-1} respectively. A concentration of 1 mg L^{-1} was chosen to establish a balance between a concentration high enough to show the adsorption potential and low enough to replicate valid concentrations of these elements in geochemical environments.

c. Solid phase

The solid phase is also known as the equilibrium phase in PHREEQC and in this study, represents soil substrates. The soil substrates were made by replicating the amount of goethite (Fe-oxide), montmorillonite (clay) and quartz (inert filler to 100%) of the average Fe-oxide and clay content of typical soils or substrates in the Witwatersrand and Karoo, respectively. Land type data from these areas were used to calculate the average Fe-oxide and clay content (Rösner et al., 1998; Land Type Survey Staff, 2000). In the Witwatersrand, the average clay content is 30.7% and Fe-oxide content is 5.7% (Rösner et al., 1998). Therefore, the substrate consisted of 30.7% clay, 5.7% Fe-oxide, and 63.6% quartz. Typical Karoo soils have an average of 15.8% clay and 0.9% Fe-oxide (Land Type Survey Staff, 2000). Thus, the soil substrate consisted of 15.8% clay, 0.9% Fe-oxide and 83.3% quartz. The molecular weight and weight percentages (Wt%) were used to calculate the mol of goethite, montmorillonite and quartz present in 250 g of the substrate. The substrate replicating the Witwatersrand soil consisted of 1.61×10^{-1} mol goethite, 1.40×10^{-1} mol montmorillonite and 2.65 mol quartz and the substrate replicating the Karoo soils consisted of 4.35×10^{-2} mol goethite, 7.19×10^{-2} mol montmorillonite and 3.47 mol quartz. In this section the pH was fixed at 2, 5, 7, and 9 respectively and gibbsite was set to precipitate.

d. Surface inputs

The surface inputs in PHREEQC approximates and replicates the adsorption sites present. There are two types of adsorption sites; strong (Hfo_sOH) and weak (Hfo_wOH) sites. In the modelling for this study, only the weak adsorption sites, represented by goethite and montmorillonite in this study, were used, because the strong sites for As and Se are not yet determined. The site densities were determined from literature, by using the fraction of montmorillonite clay minerals and Fe-oxides present in the substrate, thereafter a sensitivity analysis was done to confirm these values are as close to reality as possible (Villalobos et al., 2003; Tournassat et al., 2018). After around 25 iterations, for As- and Se contamination respectively, values converged to realise the best possible fit. Therefore, the site densities for the Witwatersrand substrate is taken as 0.881 mol sites nm^{-2} and for the Karoo substrate as 0.363 mol sites nm^{-2} (Villalobos et al., 2003; Tournassat et al., 2018). A default specific surface area of 600 m^2 g^{-1} was entered together with the mass of montmorillonite clay and Fe-oxide present in the substrate. The Karoo substrate contained 41.65 g and the Witwatersrand substrate contained 91 g of montmorillonite clay and Fe-oxides. The adsorption reactions occurred fast enough therefore reaction rates were not used or defined (Bethke, 2008).

The surface structure of montmorillonite is given in Figure 3.3. Montmorillonite clay forms part of the smectite group which is known as the 2:1 clays and has a dioctahedral crystal structure. This means that the clay consists of two tetrahedral and one octahedral structural layers. The crystal structure of montmorillonite clay was first suggested by Pauling (Occelli and Tindwa, 1983; Karthikeyan et al., 2005; Bourg et al., 2007; Maina et al., 2016). These layers together form an inner electrostatic force, termed the Stern layer. This is the layer where the exchangeable ions and pH-dependent charges occur. At low pH excess amounts of H^+ and at high pH excess amounts of OH^- ions will be present in the solution. These H^+ or OH^- ions (depending on pH) will react with the oxygens at the edge of the crystal layer through the process of protonisation (at a low pH) or deprotonisation (at a high pH), as also depicted in Figure 3.2. This process will then result in a pH-dependent charge that will impact on the adsorption of ions by montmorillonite clay (Bourg et al., 2007; Maina et al., 2016). However, montmorillonite clay has a predominantly permanent charge, caused by isomorphic substitution of Mg^{2+} and Fe^{2+} replacing Al^{3+} in the octahedral layer. This permanent charge can be as large as 95% of the total charge of montmorillonite, totally dominating the pH dependant charge (Occelli and Tindwa, 1983; Karthikeyan et al., 2005).

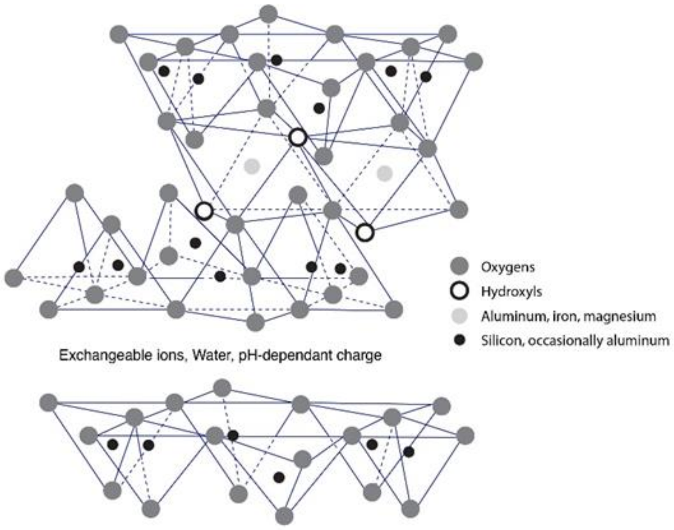

Figure 3.3 A schematic diagram of the surface structure of montmorillonite, after Maina et al. (2016).

Goethite is seen as a good adsorbent due to its highly reactive nature. It is a Fe-oxyhydroxide mineral with an orthorhombic crystal structure, which is quite abundant (Ghose et al., 2010). The surface structure of goethite is given in Figure 3.4. The process of pH-dependent charge developing on goethite is similar to that of montmorillonite. However, goethite has almost no isomorphic substitution and therefore almost no permanent charge. The ambient pH therefore largely determines the charge and sorption capacity of goethite. The hydroxide groups at the interface, or surface of the structure, are the reason for the pH-dependent charge seen at the surface of goethite. Depending on the pH and therefore the concentration of H^+ or OH^- ions in solution, the overall surface charge of goethite will change (Hiemstra and van Riemsdijk, 1996; Sun and Doner, 1996; Fendorf et al., 1997; Ghose et al., 2010; Bleam, 2017). This pH-dependent charge will control the adsorption of ions, and specifically anions such as As and Se through protonisation, by goethite (Hiemstra et al., 1989; Sun and Doner, 1996).

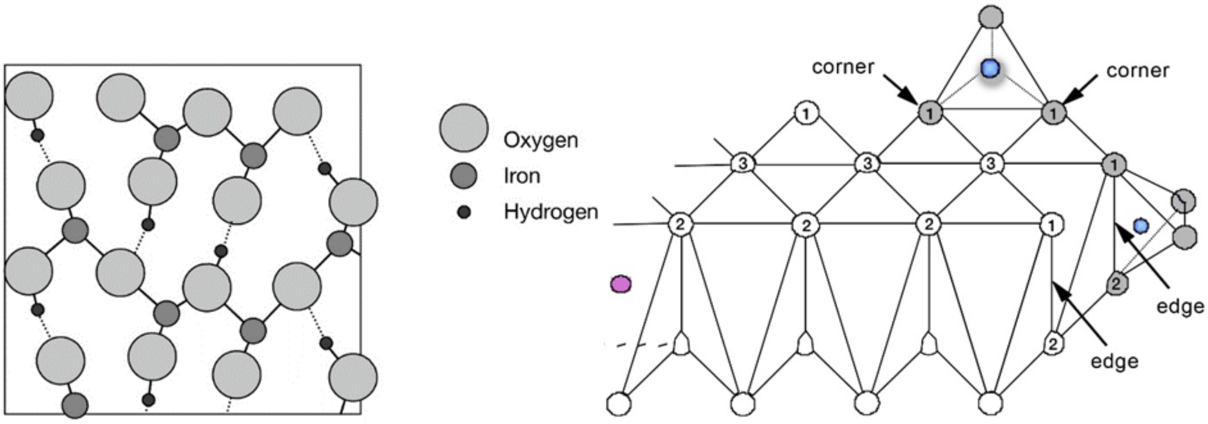

Figure 3.4 Schematic illustrations of the surface structure of goethite, after Hiemstra and Van Riemsdijk (1996).

e. Equilibrium constants

The equilibrium constants used in these models are defined by Dzombak and Morel (1990), and the log of the equilibrium constants (Log_K) of the reactions was defined in section 3.4.2.2.

3.4.2.2 Second tier model calibration and parameterisation

a. Modelled phases

The model parameterisation was used to calibrate the model to fit the experimental results done in Chapter 2. In this model calibration and parameterisation the gas, liquid, solid and surface phase inputs remain constant and the log of the equilibrium constants (Log_K) were changed.

b. Equilibrium constants

The equilibrium constants were determined by changing the Log_K of the As and Se reactions in the PHREEQC database. These reactions were:

$$\text{Hfo\_wOH} + AsO_4^{3-} + 3H^+ = \text{Hfo\_wH}_2AsO_4 + H_2O \quad (3.6)$$

$$\text{Hfo\_wOH} + AsO_4^{3-} + 2H^+ = \text{Hfo\_wHAsO}_4^- + H_2O \quad (3.7)$$

$$Hfo\_wOH + SeO_4^{2-} + 2H^+ = Hfo\_wHSeO_4 + H_2O \quad (3.8)$$

$$Hfo\_wOH + SeO_4^{2-} + H^+ = Hfo\_wSeO_4^- + H_2O \quad (3.9)$$

The specific Log_K, of a certain substrate, at a specific pH, used in calibrating the geochemical models listed in the tables below.

Table 3.1 Logarithm of the equilibrium constants (Log_K) for the As and Se reaction, at a selected pH values, for the Witwatersrand substrate.

Witwatersrand Substrate					
pH	Site Density	Log_K		Log_K	
		$HAsO_4^-$	H_2AsO_4	$HSeO_4$	SeO_4^-
2	0.881	26.81	31.00	14.05	7.05
5	0.881	26.81	31.00	11.00	9.00
7	0.881	26.81	31.00	11.00	9.00
9	0.881	24.50	30.00	13.70	11.40

Table 3.2 Logarithm of the equilibrium constants (Log_K) for the As and Se reaction, at a selected pH values, for the Karoo substrate.

Karoo Substrate					
pH	Site Density	Log_K		Log_K	
		$HAsO_4^-$	H_2AsO_4	$HSeO_4$	SeO_4^-
2	0.363	26.81	31.00	13.00	8.50
5	0.363	26.81	31.00	15.00	9.50
7	0.363	21.30	25.80	14.60	8.70
9	0.363	24.15	27.70	15.50	11.13

This second tier model calibration and parameterisation were used to build confidence in the geochemical model. Confidence in this model was built by calibrating the modelled data to fit the experimental data at the same environmental conditions. This was done by fitting the adsorption curves, from the geochemical modelling, to the adsorption curves drawn up by using experimental data (Chapter 2).

3.5 Results and discussion

3.5.1 Adsorption isotherms

3.5.1.1 Witwatersrand substrate adsorption isotherms

The measured and modelled sorption of As and Se, respectively, in a Witwatersrand substrate at a specific pH are indicated in Figure 3.5 and Figure 3.6.

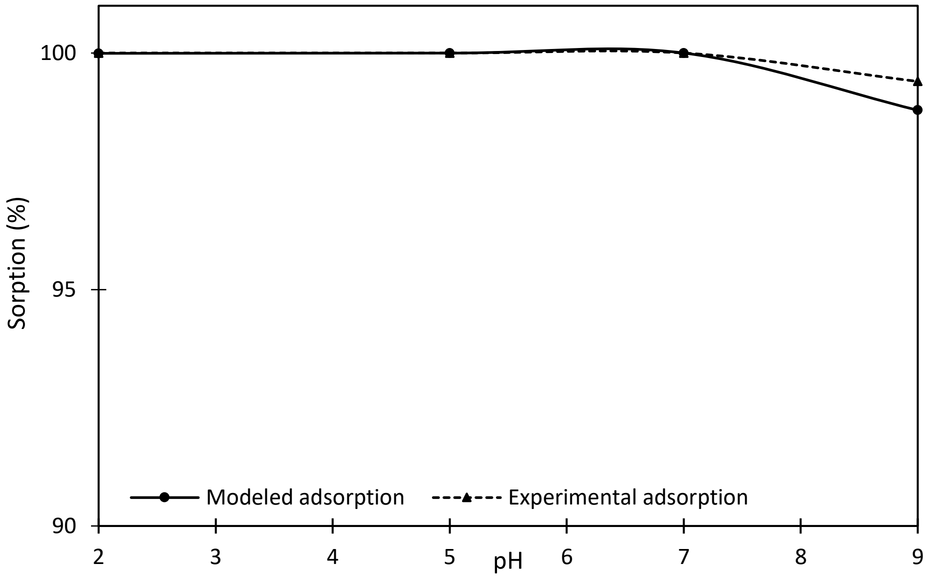

Figure 3.5 The sorption of As, at different pH values, in the Witwatersrand substrate for the calibrated modelled and for the experimentally determined sorption results.

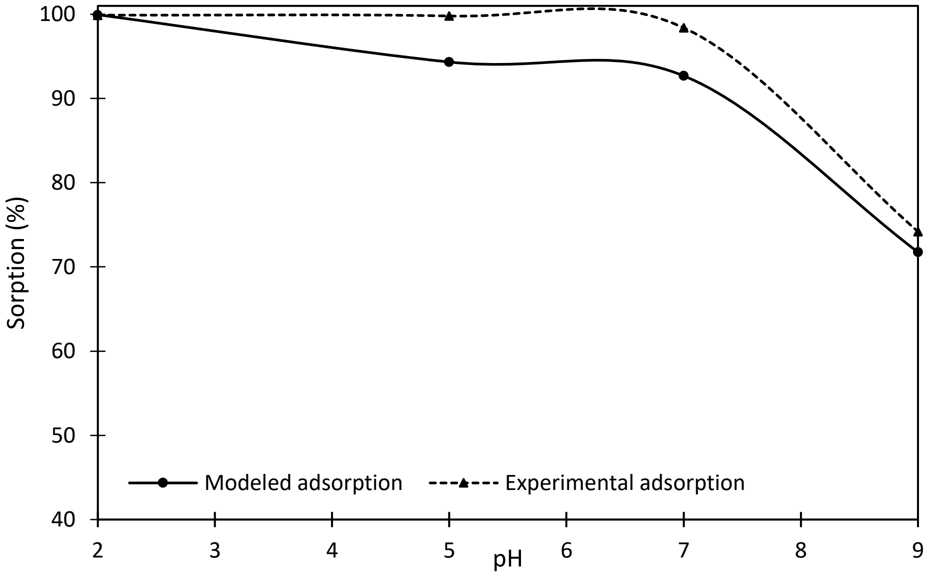

Figure 3.6 The sorption of Se, at different pH values, in the Witwatersrand substrate for the calibrated modelled and for the experimentally determined sorption results.

For this study, different scenarios were run in the modelling program PHREEQC for both the As and Se reactions at a pH of 2, 5, 7, and 9 respectively. The output values of these different scenarios were converged to achieve the best possible fit of the modelled data to the experimental data. The perfected modelled fit was found through these scenarios or iterations and the specific parameters of these iterations are given in section 3.4.2.

In the Witwatersrand substrate, it was evident that the adsorption, of both As and Se, decreased with an increase in pH. Thus, the mobility of both As and Se increased with an increase in pH, under the specific environmental conditions stated in section 4 for the

Witwatersrand prepared substrate. However, the adsorption of Se tended to be far less than the adsorption of As and the adsorption of Se also started at a lower pH (from a pH >5) than for As (from a pH >7; Figure 3.5 and Figure 3.6). This was most likely because As has a higher affinity for Fe and therefore the Fe-oxides, than what Se has (Eby, 2004). The experimental sorption was also found to be greater than the modelled sorption. This could also be due to the speciation and Log_K of As and Se that are not well understood.

3.5.1.2 Karoo substrate adsorption isotherms

The measured and modelled sorption of As and Se, respectively, in a Karoo substrate at a specific pH are indicated in Figure 3.7 and Figure 3.8.

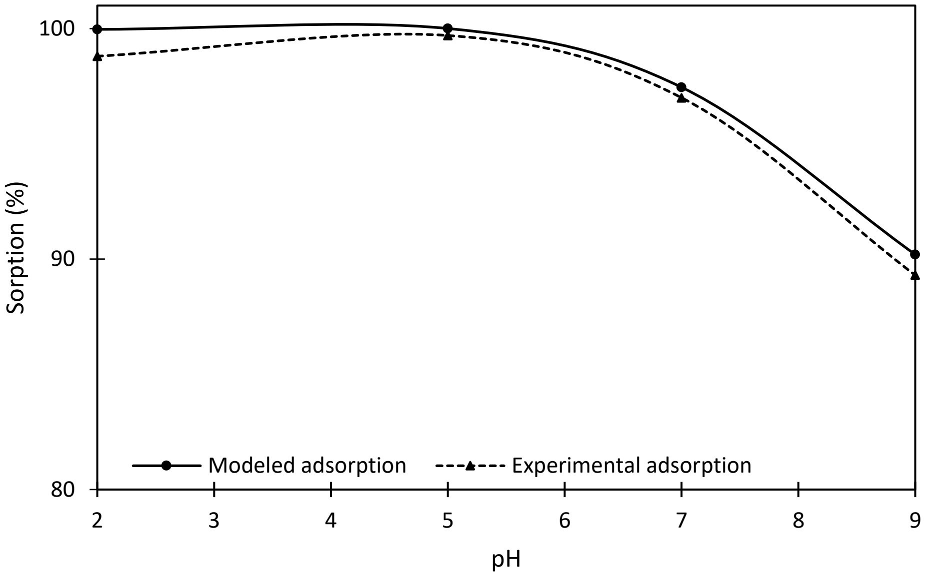

Figure 3.7 The sorption of As, at different pH values, in the Karoo substrate for the calibrated modelled and for the experimentally determined sorption results.

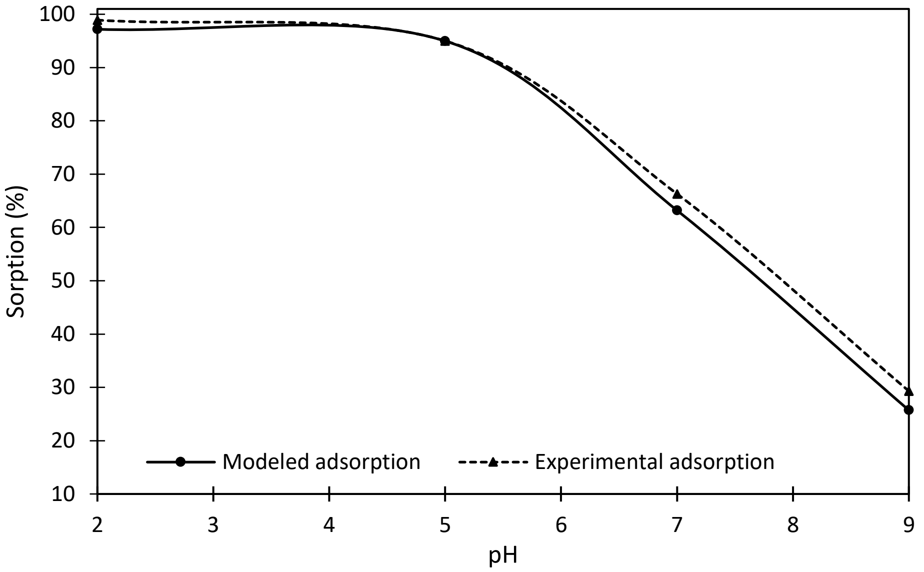

Figure 3.8 The sorption of Se, at different pH values, in the Karoo substrate for the calibrated modelled and for the experimentally determined adsorption results.

The sorption of As and Se in the Karoo substrate behaved similarly to sorption in the Witwatersrand substrate. The sorption decreases with an increase in pH and Se sorbed less at a lower pH (from a pH >5) than As (from a pH >6), meaning that Se would be more mobile than As. However, in the Karoo substrate the sorption of As started decreasing at a lower pH (a pH >6) than As in the Witwatersrand substrate (a pH >7; Figure 3.5and Figure 3.7).

Conversely, the decreased adsorption of both As and Se (up to 15% for As and 80% for Se) were greater in the Karoo substrates than in the Witwatersrand substrates (up to 5% for As and 30% for Se). This was probably due to the lower montmorillonite clay and lower Fe-oxide content of the Karoo substrate relatively to the Witwatersrand substrate (Figure 3.5 to Figure 3.8).

Small decreases in adsorption in both the experimental and modelled data at a pH <2, for both As and Se, were observed (Figure 3.7 and Figure 3.8). This was most likely due to the number of other anions present in the substrate, as a result of adding acids such as HCl (Cl^-) or H_2 SO_4 (SO_4^{2-}), that will compete for the adsorption sites on the montmorillonite clay and Fe-oxide. When the negatively charged As or Se species compete with anions such as Cl^-, the smaller anion with the larger charge density, in this case, the Cl^-, will be favoured for adsorption (Eby, 2004). However, this pH is much too low to support agronomic crop growth (Havlin et al., 2016) and should thus not be of concern in normal agronomic irrigation practices.

3.5.1.3 The behaviour of arsenic and selenium

In the geochemical modelling results, it was evident that the adsorption decreased, with an increase in pH. At acidic pH values (up to 5) As and Se were fully adsorbed and the adsorption started decreasing slowly at a pH of 5 and higher, corresponding to other studies (Plant et al., 2005). Therefore, as predicted from published literature, the sorption of the metalloid anions As and Se is pH-dependent. This was also seen from the experimental data presented in Chapter 2.

It is clear, in this specific situation, that 15% of the total As will not adsorb at high pH values in both the Karoo and Witwatersrand substrates. Thus, in these substrates and conditions, the mobilisation and leaching of As into groundwater are not of environmental concern. However, this might not be the case in certain specific situations. These may include: Firstly, soils or substrates with a lower montmorillonite clay and/or Fe-oxide content; secondly, if the concentration of As is higher; and lastly, if any of the environmental conditions differ (e.g. a reducing environment or extremely high pH). It is also important to observe and be vigilant of what the environmental impacts of irrigation with As contaminated water (onto a substrate or soil with a similar montmorillonite clay and Fe-oxide content) can be. Although, in this scenario, As will not leach in significant concentrations but can accumulate in the soil and therefore at a later stage mobilise and contaminate groundwater and/or crops when the environment or the chemical composition of the soil changes over time.

Contrary to As, a larger percentage of Se is not adsorbed (between about 30 and 80%) at a higher pH (>5). This is because As has a high affinity for Fe-oxides (siderophile). The lower percentage of adsorption results in a higher mobility of Se and therefore will be susceptible to leaching (to groundwater systems) and crop uptake. Therefore, in these specific substrates and environmental conditions, the probability of Se concentrations being higher than the threshold values present in water are substantial.

3.5.2 Equilibrium constants

To calibrate a geochemical model one of the parameters must be changed to fit the modelled adsorption isotherm to the adsorption isotherm drawn up by experimental data. The parameters that can be used to calibrate the model include the solid phase, surface inputs and equilibrium constraints. The solid phase contains the chemical composition of the substrate, which in this study is the montmorillonite clay and Fe-oxide content in the two substrates that are constant and therefore could not be changed. In the surface input, the parameterisation of the site density can be changed. However, changing the site densities of the substrates did not give the required results and by using literature to calculate the site densities provides set site densities for each substrate. As a result, at the discussed environmental conditions, pH values, and concentrations, the only parameter left is changing the equilibrium constants. The log of the equilibrium constant (Log_K) for two As and two Se species were changed and the specific details of all the equilibrium constants can be seen in the parameterisation section 3.4.2.2.

By changing the Log_K it was possible to calibrate the modelling adsorption isotherm to the experimental adsorption isotherms. However, ideally, the Log_K calculated in an experimental article given in Chapter 2 or the Log_K provided by Dzombak and Morel (1990) should suffice and the Log_K of specific As and Se species should maintain constant for all pH values. This was not the case in the geochemical modelling. This showed that this system was much more complex than a single Log_K and that the speciation of As and Se are not yet sufficiently classified. However, this was not the main focus of the study as the main focus is to determine the risk of As and Se contamination and possibly pollution. This aspect is, however, recommended for further study.

The inconsistencies of the Log_K was probably because the surface complexation is much more complex than expected. This can potentially be explained by the speciation of both As and Se that is not well defined or understood. Other species of As and Se form that are not defined in the database and are thus not calculated into the numeric model and therefore does not provide accurate results. Only two As ($H_2AsO_4^-$ and $HAsO_4^{-2}$) and two Se (SeO_4^{-2} and $HSeO_4^-$) species are defined in the database. Other species of As and Se can form and stay in solution and can, therefore, be analysed, and seem to be not adsorbed, but is not represented in the geochemical model. This might explain the inconsistencies between the modelled results with the calculated Log_K that results in a 100% adsorption and the experimental results given in Chapter 2.

3.6 Conclusions

This study has shown, and confirmed, that the adsorption of the metalloid anions As and Se decreases with an increase in pH. Thus, the decreased adsorption and mobility of As and Se increases with an increase in pH and is therefore pH-dependent. Other very important parameters controlling the decreased adsorption, excluding pH, are the site densities present in the substrate and the log of the equilibrium constant (Log_K) to define the reactions in a PHREEQC database. The unpredictability seen in the Log_K of the reactions ia because the surface complexation is much more complex than currently understood to be defined in literature (Dzombak and Morel, 1990). The surface complexation and speciation of As and Se species in geochemical environments are not distinctly described. All the As and Se species present in the system, defined in this study, are not defined in the database and is therefore not accounted for in the numeric model. All possible As and Se species defined in the database were modelled and the most probable species were then used in this study. These undefined species of As and Se can stay in solution and is analysed in the experiments but not represented in the modelling because the Log_K is not defined in the database. For example, species such as H_3AsO_4 and H_2SeO_4, which are currently not defined in the database, will be repelled by the H^+ present on the adsorption sites at a low pH leaving it in solution. There is also the possibility that some As and Se species precipitate that is also not represented by the model. Therefore, further studies should be done to establish these species and the Log_K for their reactions. This study also made it clear that thorough geochemical modelling together with applicable experimental data is a very useful tool and perspective for environmental geochemical assessment.

From this study, it is evident that irrigating with neutralised AMD or lime treated mine wastewater has its limitations and should therefore be done with circumspection. It is concluded and anticipated that, given the scope of this study, As pollution in the Witwatersrand and Karoo substrates (and therefore most likely in the Witwatersrand tailings and Karoo soils or soils with a similar clay and Fe-oxide content) is most likely not of major environmental concern since it is possible that the concentrations of goethite and montmorillonite clay present, would be sufficient to serve as a natural sorption and hence remediation thereof. However, this conclusion would still need to be determined separately for each contamination site, since the site specific conditions can change these conclusions. These results are specific and with the stated limitations and to the conditions stated in the study. These results are also assumed in scenarios where no competing anions, such as sulphate, phosphate and chloride, are present. This is also specified without acknowledging the possible outcome of As cumulative accumulation in mine tailings or soils. On the contrary, the mobility of Se observed within these substrates should be of major concern. Low adsorption and therefore high mobility of Se creates a highly probable risk for Se in the Witwatersrand tailings (or in soils with a similar composition) to leach into groundwater systems. This mobility is greater in the Karoo substrate (or soils with a similar montmorillonite clay and goethite Fe-oxide content) and therefore poses a major risk when irrigating with Se-containing treated mine wastewater, which will either be taken up by crops or might leach into groundwater systems.

Chapter 4 Synthesis

4.1 Introduction

Increases in anthropogenic activities such as mining and industrialisation during the last few decades sensitised environmentalists on the hazardous effects of these activities on natural resources and living organisms. Consequently, a substantial increase could be seen in the number of studies on the environmental impacts and rehabilitation of contaminated sites worldwide. This study focussed on the adsorption potential of the metalloid anions As and Se in constructed soil materials. The results of this and previous studies can be and is crucial in the rehabilitation of old mining sites and other contaminated soil. This can also aid in the feasibility studies being done on irrigating agricultural fields with treated mine wastewater.

Taking everything into account, the following research question was formulated: What is the adsorption potential of goethite and montmorillonite clay for As and Se, at different pH and other physicochemical conditions in soil substrates? This question was answered by conducting a laboratory experiment and through geochemical modelling. This study had two objectives: Firstly, to determine the adsorption potential of As and Se at different pH values in different soil substrates and secondly, to model the influence of pH in an oxidised environment, on As and Se adsorption in different soil substrates.

4.2 Findings

The adsorption potential of As and Se at different pH values in different soil substrates was determined by an experimental study (Chapter 2). In this chapter, the adsorption isotherms for As and Se were determined experimentally in artificially constructed Witwatersrand and Karoo substrates respectively. These adsorption isotherms showed that adsorption of As only started to decrease at a pH >7 in the Witwatersrand substrate and at a pH >5 in the Karoo substrate. While adsorption of Se started to decrease at a pH >6 in the Witwatersrand substrate and a pH >4 in the Karoo substrate.

The calculated adsorption isotherms were then used to model the influence of pH, in an oxidised environment, on As and Se adsorption in different soil substrates, by using geochemical modelling (Chapter 3). The adsorption isotherms calculated through geochemical modelling verified the results on the adsorption potential of As and Se determined in Chapter 2. However, it was evident that the speciation of As and Se, in the geochemical modelling database, were not well defined and that the species of As and Se together with the equilibrium constants of their reactions were not well defined. This was concluded after modelling the different As and Se species, and by using the most probable As and Se species in the final model. It is therefore recommended that the exact speciation of As and Se within these conditions should be determined in future studies.

This study highlighted that the decreased adsorption (and thus mobility) of both As and Se increases with an increase in pH and therefore the adsorption potential of these elements is pH-dependent. Furthermore, it was evident that the K_{eq} as well as Log_K (equilibrium constants and log of equilibrium constants) together with the site densities, had a substantial impact on the adsorption potential. It was also noted that both the speciation of As and Se within these environments and their specific K_{eq} as well as Log_K are not fully understood, further highlighting this aspect for further study.

It can be possible that all species of As and Se present in geochemical environments are not defined in the modelling database and were therefore not considered in the geochemical modelling. This can result in undetermined species of As and Se that, under these conditions, will stay in solution rather than be adsorbed. For instance, species such as $H_3AsO_4^+$ and $H_2SeO_4^+$, which are not defined in the PHREEQC database, will be repelled by the H^+ present on the adsorption sites at a low pH, leaving it in solution. There is also the possibility that some As and Se species precipitate, something that is also not accounted for in the model.

Based on the above, it was thus concluded that As mobilisation and thus leaching and contamination, at pH values <9, in Witwatersrand tailings (or a substrate or soil with a similar montmorillonite clay and Fe-oxide content) are probably not of major concern. However, this is specific to the conditions stated in this study, and for an As concentration of 1 mg L^{-1}. This is also stated without acknowledging the possible cumulative effect of As accumulation within the mine tailings or soils. Within the conditions specified for this study, it could be possible that the amount of goethite and montmorillonite clay present would be sufficient to adsorb almost all introduced As into the system. Nevertheless, this should still be determined separately for each contamination site, since the site specific conditions can greatly alter these results.

Furthermore, it was apparent that the risk for decreased adsorption and consequently the mobilisation and possible contamination of As in the Karoo substrate (or either a substrate or soil with a similar clay and Fe-oxide content) is higher than the decreased adsorption in the Witwatersrand substrate. This was attributed to the lower percentage of montmorillonite clay and Fe-oxide present in the Karoo substrate, in comparison to the Witwatersrand substrate. Consequently, when irrigating soils, similar in composition to the Karoo topsoils with rehabilitated mine wastewater containing 1 mg L^{-1} or more As close monitoring should be done to ensure that there is no As accumulation in these soils and that dangerous amounts of As are not taken up by the crops or leached into the groundwater systems.

Additionally, it was concluded that adsorption of Se decreased faster and at started at lower pH values (pH >5), than As and therefore would possibly be more mobile than As. Adsorption of Se decreased from pH values >5 in the Karoo and from pH values >7 in the Witwatersrand substrates. In the Witwatersrand tailings (or a substrate or soils with a similar montmorillonite clay and Fe-oxides) the low adsorption rates of Se put it at a possible risk for leaching into the groundwater system. This predicted low adsorption rates and implied mobility would be even greater in the Karoo substrate (or soils with similar compositions) and there is, therefore, a major risk when irrigating with wastewater (containing 1 mg L^{-1} or more Se), that Se will either be taken up by crops or will leach into the groundwater systems. In both cases the pH values of decreased adsorption correspond with soil pH values recommended for optimal crop growth (Havlin et al., 2016), putting these systems at greater risk of decreased Se adsorption and increased mobility and leaching.

4.3 Limitations and further research

When using geochemical modelling a few limitations should be considered. The first limitation was that assumptions on the precipitation of species were made based on the geochemical environment during the geochemical modelling. The possible error introduced by these assumptions was significantly reduced in this study by using the measured experimental data, which was compared to the modelled data and was then used as calibration points in the geochemical modelling. The second limitation was that the results given by the geochemical modelling represented reactions at equilibrium in "perfect" isolated scenarios with only one variable. This will hardly ever be the case in "real life" geochemical environments. However, this limitation was addressed by the use of the experimentally determined calibration points. The fourth limitation was the scant availability of thermodynamic data for the reactions of these elements. Significant limitations in the geochemical modelling also occurred due to insufficient literature on the thermodynamic equilibrium constants and the speciation of these elements within certain geochemical environments. The last limitation was that the Fe-oxide and clay sorption sites, in terms of specific surface area (SSA) and point of zero charge (PZC), was determined from literature. Future studies should consider determining these through fully characterisation.

Therefore, determining the speciation and defining the species of As and Se and the equilibrium constants of the reactions present in different geochemical environments are recommended for future research. A further recommendation, although not a major finding emanating from this study, would be to determine and define soil screening values for Se due to the apparent risk of Se contamination identified through this study.

4.4 Conclusions

Based on the results obtained through this study it was concluded that no more than 15% of As was not adsorbed at a pH value of 9. Thus, the decreased adsorption and therefore mobility of As, at an agronomic high pH (8-9), in the Witwatersrand and Karoo substrates should not be of major environmental concern. However, this is specific to the conditions stated in this study and is stated without acknowledging the possible cumulative effect of As accumulation within mine tailings or soils.

Furthermore, it was concluded that Se would be much more mobile than As and between 30% and 80% of Se was not adsorbed in the Karoo and Witwatersrand substrates respectively, at pH values between 5 and 9. The decreased adsorption of Se started at pH values >5 in the Karoo substrate and pH values >7 in the Witwatersrand substrate. The low adsorption rates of Se at agronomic higher pH values of 5 to 9 thus creates the probable risk for leaching thereof into groundwater systems or for crop uptake. Irrigation with Se-containing wastewater is therefore not recommended on soils similar to those of the Witwatersrand and Karoo substrates since these are also the agronomic pH values recommended for optimal crop growth.

In closing, this study demonstrated that comparative geochemical modelling, combined with relevant independent experimental data, is a valuable method for environmental geochemical assessments.

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Chapter 6 Appendix

Table 1: Raw data for the Witwatersrand and Karoo prepared substrates.

Witwatersrand substrate									
	pH	Sample and replication			Ave	Standard error	Ave in Solution	[ ] Adsorption	% Adsorption
		1	2	3					
As	2	0,001	0	0	0,000333	0,000333333	0	1	100
	5	0	0	0	0	0	0	1	100
	7	0,001	0	0,001	0,000667	0,000333333	0	1	100
	9	0,007	0,006	0,004	0,005667	0,000881917	0,006	0,994	99,4
Se	2	0,001	0,001	0,002	0,001333	0,000333333	0,001	0,999	99,9
	5	0,003	0,002	0,002	0,002333	0,000333333	0,002	0,998	99,8
	7	0,017	0,012	0,018	0,015667	0,001855921	0,016	0,984	98,4
	9	0,222	0,168	0,384	0,258	0,064899923	0,258	0,742	74,2

Karoo substrate									
	pH	Sample and replication			Ave	Standard error	Ave in Solution	[ ] Adsorption	% Adsorption
		1	2	3					
As	2	0,011	0,012	0,013	0,012	0,00057735	0,012	0,988	98,8
	5	0,002	0,003	0,003	0,002667	0,000333333	0,003	0,997	99,7
	7	0,027	0,044	0,019	0,03	0,007371115	0,03	0,97	97
	9	0,114	0,15	0,056	0,106667	0,02738207	0,107	0,893	89,3
Se	2	0,011	0,009	0,013	0,011	0,001154701	0,011	0,989	98,9
	5	0,046	0,051	0,052	0,049667	0,001855921	0,05	0,95	95
	7	0,37	0,246	0,396	0,337333	0,046279345	0,337	0,663	66,3
	9	0,704	0,729	0,688	0,707	0,011930353	0,707	0,293	29,3