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Mobility and Transformation of Inorganic Contaminants in Mining-impacted Groundwater

Anita Etale and Sabelo Mhlanga

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Abstract

Mining often results in the contamination of groundwater by metal, sulphate and radionuclide ions following their percolation from tailings impoundments. This chapter discusses the processes by which elements within tailings are transformed and translocated to groundwater and the role of aquifer characteristics and colloids in these processes. The prevention and remediation of contaminated groundwater is also discussed, with particular attention given to the use of permeable reactive barriers and sulphate reducing bacteria.

Keywords: colloidal transport, acid mine drainage, inorganic contaminants, groundwater remediation, permeable reactive barriers, sulphate reducing bacteria

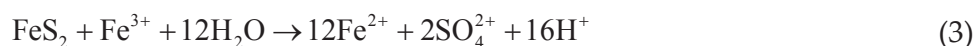
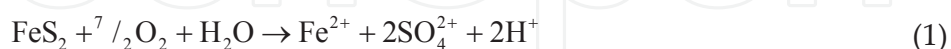
1. Introduction

Mining has been the mainstay of many economies across the globe for centuries. There is evidence, for example, of copper mining in Cyprus from as early as 4000 BC and from the Rio Tinto deposits in Spain from 1200–1500 BC [1]. However, along with the economic growth spurred by mining came unprecedented environmental pollution. The contamination of water resources by high concentrations of metals, non-metals and radionuclide elements has been reported from Spain and Portugal [2], to Australia [3] and South Africa [4]. Groundwater may be contaminated by direct infiltration of leachate from mine tailings and other mine wastes or following underground disposal of mine wastes [5]. Contaminated groundwater then recharges surface water with acidic metal-laden water (acid mine drainage) (**Figure 1**).



Figure 1. A river in the west of Johannesburg, South Africa, contaminated by acid mine drainage from disused underground mines. Note the orange colour which is due to deposition of iron flocs on the river bed.

Acid mine drainage (AMD) is formed via a cascade of reactions (Equations 1–4) when sulphide minerals are exposed to oxygen by mining [6]. The process begins when oxygenated water percolates through the finely divided tailings and pyrite is oxidised to ferrous iron (Equation 1) and then to ferric iron (Equation 2). Ferric iron which is soluble at pH below 3.5 then acts as an additional oxidising agent for pyrite (Equation 3). Above pH 3.5, ferric iron precipitates as $\text{Fe}(\text{OH})_3$ (Equation 4); a reaction that is able to buffer the pH of AMD at pH 2.5–3.5 [7].



This sustained acidity leads to the dissolution of other sulphide ores hence the presence of ions including Ag, Au, Cd, Co, Mn, Ni, Hg, Mo, Se, U, Th and Zn in mine drainage [4] and metal-laden water percolates through the tailings heaps to recharge groundwater. A conceptual model of this process was supplied by Tutu et al. [4] (**Figure 2**). In this model, ingress through the dump by oxygenated water results in the oxidation of tailings and the dissolution of elements followed by a downward movement of these dissolved ions into groundwater. This chapter focuses on the transformation and mobility in groundwater, of inorganic contaminants originating from mining activity. Here, groundwater encompasses water in aquifers below tailings dumps as well as that in pores within tailings (pore water).

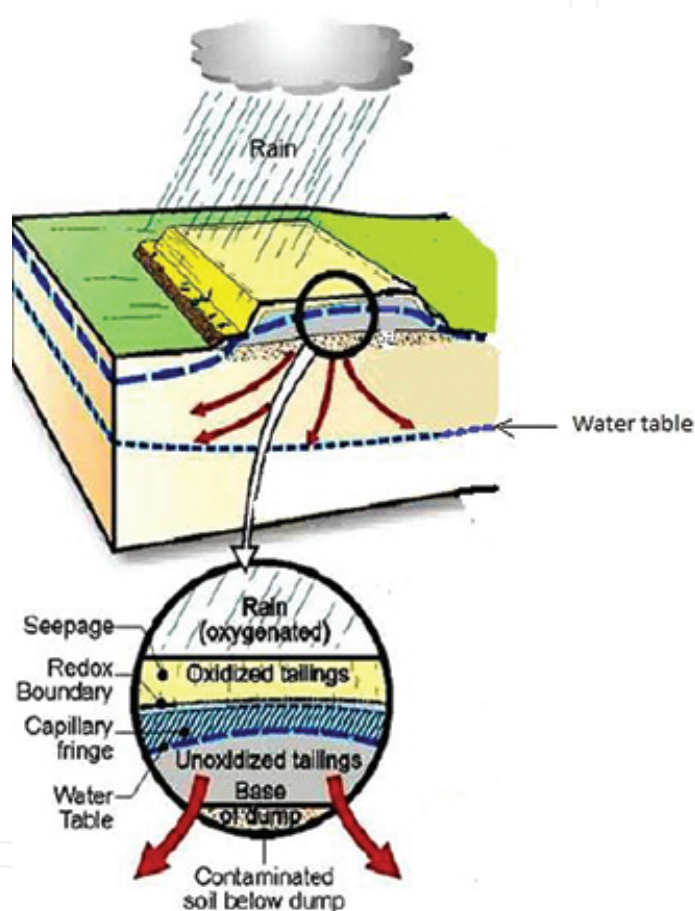


Figure 2. A conceptual model of the downward movement of elements through tailings dumps into groundwater (After [4]).

2. Transformation of inorganic contaminants in groundwater

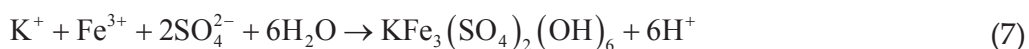
The transformation of inorganic contaminants in groundwater is influenced by a number of chemical and physical characteristics of aquifers such as pH, redox potential (Eh) and organic matter [8]. These properties have an influence over contaminant transformation reactions

including precipitation/co-precipitation-dissolution, oxidation-reduction and acid–base/sorption–desorption [9].

2.1. Precipitation/dissolution

Precipitation/co-precipitation and dissolution reactions play an important role in determining elemental concentrations in groundwater. Jean and Bancroft [10] showed, using pyrite (FeS), sphalerite (ZnS), galena (PbS) and pyrrhotite (Fe_{1-x}S), that sulphide minerals are excellent scavengers for dissolved Hg²⁺, Pb²⁺, Zn²⁺ and Cd²⁺ ions, acting as adsorbents for these metals. However, Özverdi et al. [11] reported that under acidic conditions (< pH 3), metal removal by pyrite was by precipitation of metal sulphides due to the presence of H₂S. In contrast, metal hydroxides were precipitated under basic conditions. These observations were supported by the field studies of Muller et al. [12] in the Kristineberg mines in Sweden and Al et al. [13] in the Kidd Creek tailings impoundment in Ontario, Canada, which that both adsorption and precipitation reactions were responsible for metal attenuation.

Ferric iron is ubiquitous in AMD-contaminated environments. Its precipitation via various pathways (Equations 5–7) is a significant process in the attenuation of metal on concentrations in mine drainage via co-precipitation reactions [14]. Indeed, Fe- and Al-compounds are commonly used for the chemical precipitation of As(III) and As(V) in water treatment plants [15].



Ferrous iron, on the other hand, is controlled by the precipitation of siderite (FeCO₃) (Equation 8), a reaction occurring mainly in shallow tailings.



Elemental concentrations are also controlled by simple precipitation reactions in response to solution pH through the formation of insoluble hydroxides such as Pb(OH)₂ and Cu(OH)₂ or following reaction with sulphides and carbonates to form insoluble compounds [11].

With respect to dissolution, McGregor et al. [16] found that Ca and Mg concentrations in the Copper Cliff tailings in Ontario, Canada, were controlled by the dissolution of carbonate and aluminosilicate minerals during pH buffering reactions. Similarly, Mn was derived from the dissolution of pyroxene, chlorite, amphibole or carbonates, Al and Si from weathering of

biotite, orthopyroxene and feldspars and Ni and Zn concentrations from the oxidation and dissolution of pentlandite ((Fe,Ni)₉S₈) and sphalerite (ZnS). K and Na on the other hand were controlled by dissolution of aluminosilicate minerals although their concentrations were limited by equilibrium with respect to jarosite (KFe₃(SO₄)₂(OH)₆) and natrojarosite (NaFe₃(SO₄)₂(OH)₆). Dissolution may also be microbially-driven. Cummings et al. [17] reported the release of arsenate following the dissolution of scorodite (FeAsO₄·2H₂O) by an iron-reducing bacterium, *Shewanella alga*.

2.2. Oxidation–reduction

Oxidation–reduction reactions may be chemically- or biologically-driven [18]. Selenate (SeO₄²⁻) may be reduced to elemental selenium (Se⁰) by ferrous hydroxide [19] and zero-valent iron (ZVI) has been used for the reductive precipitation of As from contaminated water [20]. Microbial oxidation-reduction in some cases can be many times faster than abiotic reactions [21]. The oxidation of As(III) to As(V) by a *Thermus* species, for example, was found to be approximately 100 times faster than abiotic rates [22].

Redox states of As have environmental implications because of their effect on As speciation. As(V), the predominant form in aerobic environments, is more strongly sorbed to mineral surfaces and thus less mobile than As(III) which sorbs less strongly and is thus more mobile [23]. Routh et al. [24] conducted microcosm experiments to investigate As behaviour in mine tailings near the Adak mine in northern Sweden. They found that microbial reduction of As(V) to As(III) increased the concentrations of the latter in aqueous media and as such, enhanced As remobilisation from sediments. In contrast, As(V) concentrations increased in sediments and aqueous media of control experiments treated with formaldehyde and HgCl₂.

Treatments applied to mine tailings may also have an effect on microbial activity and As behaviour in mining-impacted environments. Macur et al. [25] reported that the addition of lime (CaO), a common treatment applied to mine tailings to immobilise metal ions, stimulated As-reducing microorganisms (*Caulobacter*-, *Sphingomonas*- and *Rhizobium*-like populations) and in turn, enhanced As(V) reduction and mobilisation in tailings.

Fe, an important variable in mining-impacted environments, also influences As mobilisation. Han et al. [26] reported that Fe(II) significantly inhibited the removal of As(III) by MnO₂ in acidic environments (pH 3). They postulated that ferric iron compounds formed a coating on MnO₂ surfaces which inhibited access of As(III) ions to oxidation sites on MnO₂. The inhibition was however dependent on how Fe(II) ions were introduced into the system. Where the MnO₂ was pre-treated with Fe(II), As(III) diffused through the schwertmannite coatings that formed on the MnO₂ and its oxidation to As(V) was possible. However, where Fe(II) and As(III) were introduced simultaneously, competitive oxidation of the two ions prevented the complete oxidation of As(III) due to the formation of FeOHAs or FeAsO₄ coatings on the MnO₂ surface.

Cr exists mainly as Cr(III) and Cr(VI). Cr(VI) is highly soluble and therefore more mobile while Cr(III), tends to precipitate as amorphous hydroxides e.g. Cr(OH)₃ and ((Fe,Cr)OH)₃ in slightly acidic and alkaline environments. Cr(III) is commonly oxidised to Cr(VI) by manganese oxides.

In fact, manganese oxides are the only naturally-occurring inorganic phases capable of this reaction [27, 28] which Weaver and co-workers [29] found proceeded in multiple stages. However, Eary and Rai [28] reported that Cr(III) oxidation by pyrolusite (β - MnO_2) was slow in both acidic and slightly acidic solutions. In an acidic solution, slow oxidation was likely the result of the strong sorption of the oxidation product, Cr(VI), to the pyrolusite surface. Such sorption limited contact of unoxidised species with the pyrolusite surface, inhibiting additional oxidation [30]. In slightly acidic to basic media, slow oxidation was the result of the low solubility of $\text{Cr}(\text{OH})_3$. Clearly, the equilibrium favoured the trivalent ion. Nevertheless, as with As, a suite of reducing microorganisms exist for reduction of Cr(VI) to Cr(III). Native isolates of *Acinetobacter* sp. from the Sukinda Valley in Jaipur, India were able to reduce initial Cr(VI) concentrations of 5 mg L^{-1} by 80% in 7 hours [31]. Similar results were reported by Dhal et al. [32] using a *Bacillus* sp. bacterium from chromite mine soils in Boula-Nuasahi mine in Orissa, India. The strain reduced > 90% of 100 mg L^{-1} Cr(VI) in 144 hours at pH 7 and 35°C .

2.3. Acid–base/sorption–desorption

Variable charge/amphoteric minerals such as crystalline and short-range ordered Fe-, Al-, and Mn- significantly influence the concentrations of elements in groundwater through adsorption/ion exchange reactions. This is because of (i) their large surface areas (ii) the acid–base surface hydroxyl groups resulting from the dissociative chemisorption of water molecules on their surfaces [33, 34]. Surface functional groups on mineral oxides undergo protonation (Equation 9) and deprotonation (Equation 10) reactions depending on solution pH [35]. As such, oxide surfaces are positively charged and primed for anion adsorption at lower pH values and negatively charged and primed for cation sorption at higher pH values [35, 36].



Adsorption of ions from solution (**Figure 3**) is therefore a bid to maintain electric neutrality both on the oxide surface as well as in the solution (ion exchange) [36].

The adsorption of divalent ions to oxide surfaces including goethite, hydrous iron and manganese oxides has been reported in several studies. Borah and Senapati [37] investigated the factors influencing the adsorption of Cd^{2+} to natural pyrite. They found that metal uptake increased with decreased pyrite particle size and was maximal at 30°C and pH 6. At this pH, Cd^{2+} ions were the main ions in solution and metal uptake was thus an exchange between the H^+ and Cd^{2+} ions on the pyrite surface. Similar findings were reported by Forbes et al. [38] in the adsorption of Cd^{2+} , Co^{2+} , Pb^{2+} , and Zn^{2+} on goethite and by Gadde and Laitinen [39] in the adsorption of Pb^{2+} , Cd^{2+} , Zn^{2+} and Tl^+ onto hydrous iron and manganese oxides. Ion exchange may also occur with fixed charge minerals such as zeolites where contaminated water comes into contact with clay minerals [40–42]. Adsorption is not always accompanied by proton loss. In the adsorption of arsenate to goethite, for example, $\text{FeAsO}_4\text{H}_2^0$ and FeAsO_4H^- were the

dominant species at pH < 5 and pH 5–8 respectively, in reactions that were not accompanied by the loss of protons from the goethite surface [35].

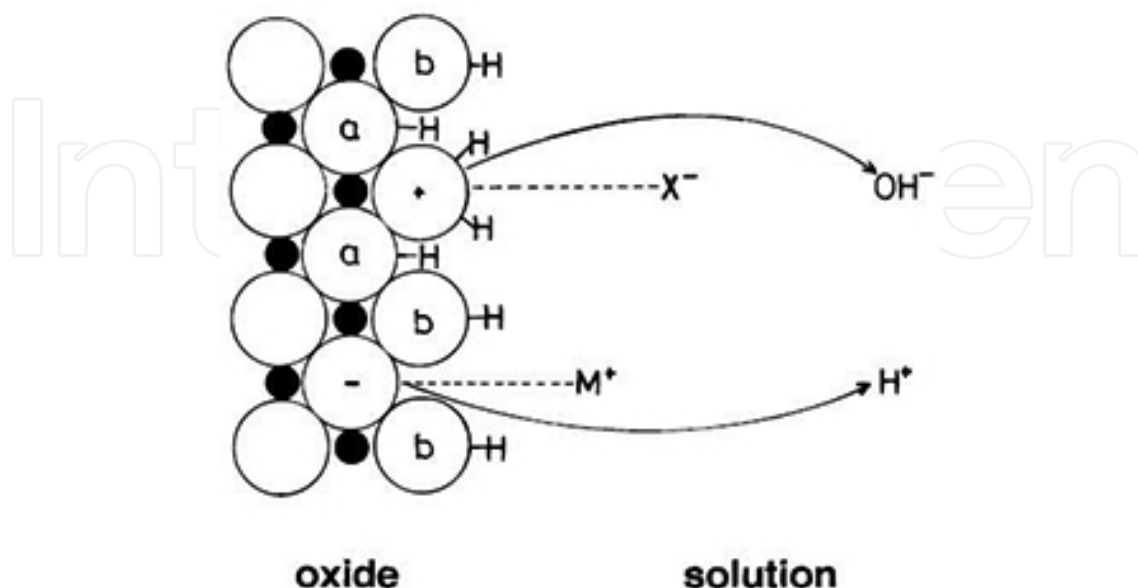


Figure 3. Acid and base hydroxyl sites on metal oxide surfaces and ion exchange reactions at the oxide-solution interface: ●=metal ions, ○=oxide ions, a=acid hydroxyl sites and b=base hydroxyl sites [36].

Determining the mode of contaminant binding is essential to predicting their behaviour in groundwater. Contaminants may be sorbed by electrostatic, hydrogen or covalent bonds. Electrostatic bonds are formed between charged hydrated species and oppositely charged mineral surfaces forming weak outer-sphere complexes. Contaminants sorbed in this way are easily desorbed by perturbations in solution parameters e.g. pH, ionic strength. Hydrogen bonds have intermediate strength while covalent bonding results in strong sorption of contaminants. Contaminants sorbed this way are harder to desorb and colloidal transport may play an important role in their transport through groundwater.

3. Mobility of inorganic contaminants in groundwater

The mobility of contaminants in groundwater has been the subject of many investigations. Early models of contaminant mobility divided contaminants between only two phases: the dissolved phase (mobile) and a sorbed phase (immobile). However, after contaminants were detected at distances further than was predicted by this model, a third phase, the mobile colloidal phase, was applied (**Figure 4**) [16, 33, 43–47]. Buddemeier and Hunt [48] found that colloids were responsible for the transport of Mn, Co, Ce and Eu from the Nevada ammunitions test site to a location 300 m away from the disposal site. Similar findings were made by Kersting et al. [47] for the transport of Pu from the same site and by Hochella et al. [49] for the transfer of As, Cu, Pb and Zn from the largest Superfund site in the USA.

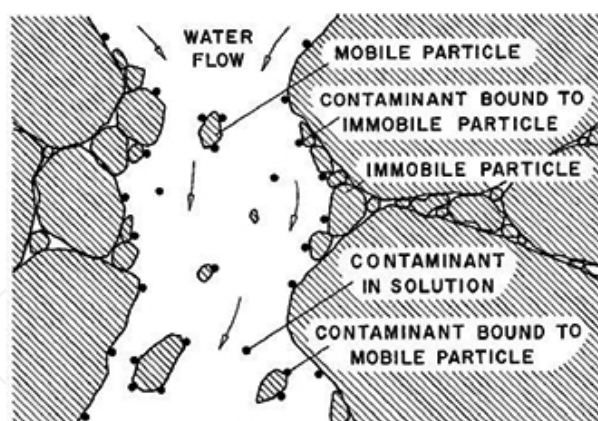


Figure 4. Schematic representation of colloid facilitated transport in a subsurface water-saturated medium. Contaminants (●) are either dissolved in solution, adsorbed to mobile phases (colloids) or to stationary phases [50].

For colloid-facilitated contaminant transport to be efficient, three criteria must be met: (i) colloids must be generated, (ii) a strong association must be formed between contaminants and the colloids, (iii) the colloid-contaminant composites must be transported through groundwater [50, 51]. Colloids are particles in the 1 nm to 1 μm size range [52]. They may be organic e.g. humic acids and microbes or inorganic e.g. metal oxy(hydr)oxides, carbonates, silicates and phosphates [52–54]. Inorganic colloids are particularly important in mining-contaminated groundwater. In these environments, colloids may be formed biogenically, as a result of ore processing or by precipitation from supersaturated solutions [53, 55]. Webster et al. [54] suggested that colloids formed in AMD were more effective sorbents than pure minerals due to the presence of sulphates and the influence of bacterial activity on their synthesis. Colloids may also be mobilised by perturbations to groundwater properties including pH, ionic strength and flow velocity (e.g. flow through fractures or variable infiltration following rainfall events). pH shifts are especially important in AMD-impacted environments as pH influences the formation of Fe and Al colloids [53, 56]. It also influences colloidal surface charges, the affinity of contaminants for colloid surfaces and the suspension or precipitation of colloids.

Solution ionic strength also influences colloid mobilisation due to its effect on the electric double layer of ions as put forward in the DVLO (Derjaguin-Landau-Verwey-Overbeek) theory. According to this theory, colloid mobilisation increases with decreasing ionic strength because the electrostatic double layer around colloids expands resulting in greater repulsion between like-charged colloids. Thus, ^{137}Cs by kaolinite through quartz found that transport was substantially increased at low ionic strengths because kaolinite colloids were more mobile and bound more ^{137}Cs . [57]. Increases in ionic strength on the other hand, lead to compression of the double layers, hence a decrease in repulsive forces and colloid aggregation/coalescence [58, 59]. Thus, contaminant transport may be retarded due to colloidal sedimentation. Kimball et al. [56] found that while Fe colloids aided the transport of As, Cd, Cu, Mn, Pb and Zn from mining flows, the colloidal load decreased by half after the first 50 km due to aggregation and sedimentation of colloids in the stream bed. Retardation may also be due to colloidal plugging/blockage of pores [60] within transport matrices.

4. Prevention and remediation of groundwater contamination by AMD

Conventional methods of AMD treatment involve the hydroxide precipitation using quicklime (CaO), hydrated lime (Ca(OH)₂), caustic soda (NaOH) or soda ash (Na₂CO₃) [9] or sulphide precipitation agents such as NaS, NaHS, BaS, FeS or H₂S [61]. This latter approach is superior because metal sulphides are generally less soluble than hydroxide counterparts, and as such, allows more complete precipitation (although the objectionable odour and toxicity of H₂S has to be considered).

Iron, in its reduced form, either as ferrous salts or zero valent form, has also been used for the chemical treatment of contaminated water. The primary advantages associated with ZVI use include low cost, simplicity in handling and the formation of strong complexes between contaminants and the iron oxides [62]. Farrell et al. [20] and Melitas et al. [63] applied ZVI for the removal of arsenate ions from solution. Adsorption was resolved as the removal mechanism because no As(III) was detected in solution. ZVI was also effective for the removal of CrO₄²⁻, TcO₄⁻, MoO₄²⁻ and UO₂²⁺ ions by reductive precipitation [26, 62, 64–67]. The rate of removal followed the order CrO₄²⁻ > TcO₄⁻ > UO₂²⁺ >> MoO₄²⁻ with CrO₄²⁻ concentrations decreasing from 10,000 µg L⁻¹ to < 5 µg L⁻¹ in 1 hour [65]. Cationic contaminants e.g. Ag⁺ and Hg²⁺ may also be reduced to their zero valent metallic forms [68]. The use of ZVI exploits redox reactions and the strong reducing properties of iron to convert contaminants into less soluble immobile forms [63]. In this process, ZVI is first oxidised by water to Fe(II) which then acts as an electron donor for the reduction of dissolved ions (Equation 11) [20, 69].



With the advent of nanotechnology, nanoscale ZVI (nZVI) use has also been attempted in laboratory and field studies [70, 71]. Li et al. [72] reported that for Cr(IV) degradation, reaction rates for nZVI were at least 25–30 times faster and the sorption capacity was much higher compared with granular iron. In another study, 25% of As(V) was reduced to As(III) after 90 days [73]. Despite this, the environmental and human health risks associated with nanoparticles have meant that larger scale application of these materials has been approached with caution. Tratnyek and Johnson [74], however, pointed out that the mobility of nanoscale ZVI was less than a few metres under almost all relevant environmental conditions and thus, human exposure was likely to be minimal.

Sulphate reducing bacteria (SRB) have been increasingly investigated for mine drainage remediation since Tuttle et al. [75] documented sulphate reduction in an AMD-contaminated stream. Samuel et al. [31] reported the remediation of Cr(VI) by indigenous isolates of *Bacillus*, *Acinetobacter* and *Escherichia* spp. from chromite mines in the Sukinda Valley of Orissa, India. SRB utilize organic carbon or hydrogen to reduce sulphates to sulphides (Equation 12) which then facilitate the precipitation of metal sulphides (Equation 13). This reaction also increases the alkalinity and pH of solutions, further promoting metal precipitation [76]. As such, the use

of SRB for AMD treatment reduces sulphate concentrations, precipitates metal ions from solution and raises solution pH.



Cardenas et al. [77] reported the biological in situ remediation of uranium contaminated groundwater. The growth of denitrifying, Fe(III)-reducing and SRB including *Desulfovibrio*, *Geobacter*, *Anaero- myxobacter*, *Desulfosporosinus*, *Acidovorax*, *Ferribacterium* and *Geothrix spp* through weekly injections of ethanol into the subsurface. After 2 years, U concentrations were reduced from 60 mg L⁻¹ to < 30 µg L⁻¹. Sulphate concentrations also decreased when ethanol was injected and rebounded when injection stopped, indicating SRB activity in the subsurface.

Such in situ approaches for the treatment of mine drainage contamination have attracted much attention in recent times. Designed to intercept contaminants in the subsurface with reactive materials, in situ treatment has the advantage of treating contaminated groundwater prior to the oxidation of Fe²⁺ (Reaction 2), thus preventing the generation of additional acidity and mobilisation of additional metal ions [64]. Sulphate reduction is also optimised in the near-neutral pH characteristic of many aquifers and the process is less costly because the volumes of water to be treated are lower than in pump-and-treat systems [78]. Two possible approaches exist for *in situ* remediation. The first involves injecting reactants into the subsurface to form a reactive treatment zone in which reactants are adsorbed onto aquifer materials (**Figure 5a**). The procedure by Cardenas et al. [77] described above falls in this category. Alternatively, permeable reactive barriers may be keyed in to underlying bedrock in the flow path of contaminants (**Figure 5b**).

A number of studies have documented the use of PRBs for the remediation of AMD-contaminated groundwater [64, 78, 79]. The reactive materials within PRBs may be chemical or biological [80]. Baker et al. [81] used a mixture containing 50 wt% silica sand, 45 wt% crushed limestone and 5 wt% metal oxide for the removal of phosphates while ZVI, FeCO₃, FeS were investigated for Cr(VI) removal [82]. Biologically-driven PRBs (biobarriers) mostly comprise of SRB [61, 83] and require (i) an anaerobic environment (redox potential of ~200 mV), (ii) pH values greater than 5, (iii) a sulphate species to be reduced and (iv) an energy source (electron donor), mostly short chain organic substrates e.g. ethanol although a variety of natural substrates including leaf mulch, vegetal compost and sawdust [84] have been tested. Benner et al. [85] installed a PRB 20 m long, 4 m thick and 3.5 m tall into the Nickel Rim aquifer downstream of a tailings impoundment. They recorded, after 22 months, dramatic changes in the concentrations of several contaminants. Concentrations of sulphates, Fe and Ni decreased by 2000–3000 mg L⁻¹, 270–1300 mg L⁻¹ and 30 mg L⁻¹, respectively. In addition, alkalinity increased by 800–2700 mg L⁻¹ and the populations of SRB were 10,000 times greater than before the installation of the PRB. Column experiments by Waybrant et al. [86] showed similar results: iron concentrations decreased from 300–1200 mg/L to <0.01–220 mg/L while Zn and Ni

decreased from 0.6–1.2 mg L⁻¹ to 0.01–0.15 mg L⁻¹ and 0.8–12.8 mg L⁻¹ to <0.01 mg L⁻¹, respectively. The pH increased slightly from 5.5–6.0 to 6.5–7.0 and alkalinity from <50 mg/L to 300–1300 mg L⁻¹. Biobarriers are also effective for the attenuation of Cr(VI) [87] radionuclide ions [88] and sulphates [89]. Sulphate concentrations were decreased from 1800 to <250 mg L⁻¹ and the mine waters neutralised using only bacterially-mediated alkalinity. Natural treatment as

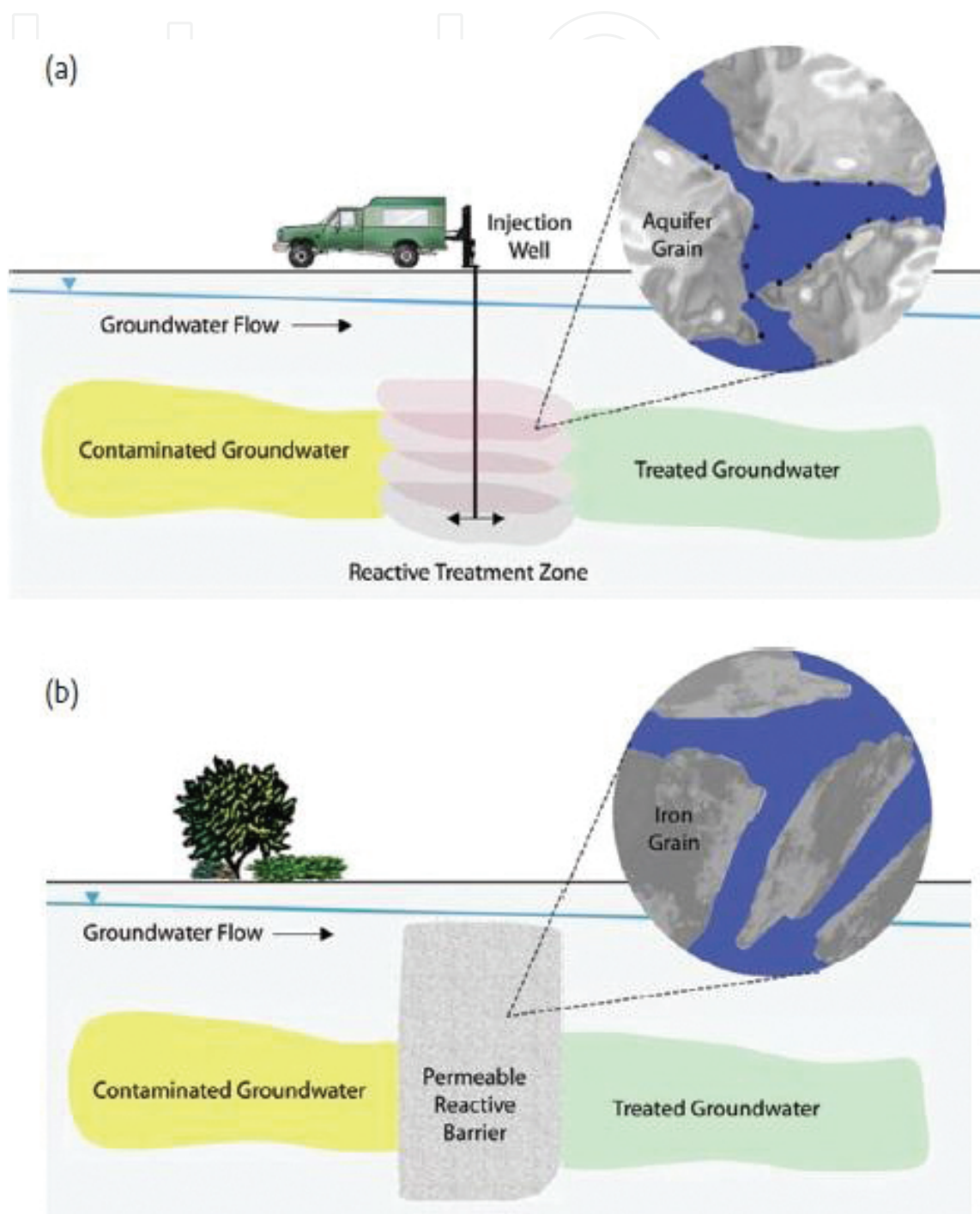


Figure 5. In situ treatment of groundwater may be by a reactive treatment zone (a) or a permeable reactive barrier (b) (After [74]).

well as permeable reactive barriers therefore both hold promise for the treatment of groundwater contamination. Future research should look into the incorporation of nanomaterials e.g. embedded in polymers, into PRBs to facilitate faster reaction times and more efficient removal of contaminants.

5. Conclusions and recommendations

This chapter explored the behaviour of inorganic contaminants from mining activity, in groundwater. The processes influencing their transformation i.e. acid/base, redox and (co)precipitation/dissolution reactions have been discussed in detail. The factors influencing their mobility, specifically, the role of colloids as well as the prevention and remediation of contamination have also been reviewed. Because of their low costs and preclusion of the need for pumping out aquifers, PRBs remain a viable option for the prevention and treatment of contaminated groundwater. Future research should look into the use of nanomaterials in PRBs. With their large surface areas and faster reaction rates, the use of nanomaterials in PRBs will likely result in greater treatment efficacy. Although the current high cost of some nanomaterials may hinder their application, this will be achievable as production technologies improve and prices decrease. On the other hand, the use of SRB in PRBs may provide a more natural alternative devoid of the environmental concerns associated with the introduction of engineered nanomaterials to the environment. It also has the double advantages of removing both metal and sulphate ions. Research into the use of SRB in PRBs will involve identification and isolation of bacterial strains suited for each contaminated site as studies have shown bacteria to be site specific and not transferable.

Author details

Anita Etale* and Sabelo Mhlanga

*Address all correspondence to: aetale@gmail.com

Nanotechnology and Water Sustainability Research Unit, College of Engineering, Science and Technology, University of South Africa, Florida Campus, Johannesburg, South Africa

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