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Metallic Iron for Safe Drinking Water Production

38 pages, 2 figures, 151 references

This work is dedicated to
my grandmother,
my parents,
my brothers and sisters,
my wife,
my children
for their endless love.

"**An error does not become truth by reason of multiplied propagation, nor does truth become error because nobody sees it.**" Mahatma Gandhi

Conseil à un jeune homme inconnu

Alfred de Vigny (27.03.1797 – 17.09.1863)

"Conseil à un jeune homme inconnu" is the sub-title of "La Bouteille à la Mer", a poem by Alfred de Vigny.

The symbol in "La Bouteille à la Mer" is that of a vessel wrecked off the Straits of Magellan; the captain realising that the ship is sinking writes in haste a warning to future sailors, puts the precious document into a corked bottle and throws it out to sea. The ship sinks together with the captain and crew. The fragile bottle then becomes the hero of the poem, and is cast up finally on the shores of France (Rooker 1914, Morton Dey 1936).

When the vessel sinks and the captain goes down with it, he throws the bottle into the sea.

Il sourit en songeant que ce fragile verre
Portera sa pensée et son nom jusqu'au port ;
Que d'une île inconnue il agrandit la terre ;
Qu'il marque un nouvel astre et le confie au sort ;
Que Dieu peut bien permettre à des eaux insensées
De perdre des vaisseaux, mais non pas des pensées,
Et qu'avec un flacon il a vaincu la mort. (Strophe XV)

A fisherman on the coast of France catches the bottle in his nets; he does not dare open it, but takes it to a savant to find out what "this black and mysterious elixir " is:

Quel est cet élixir ? Pêcheur, c'est la science,
C'est l'élixir divin que boivent les esprits,
Trésor de la pensée et de l'expérience ;
Et si tes lourds filets, ô pêcheur, avaient pris
L'or qui toujours serpente aux veines du Mexique,
Les diamants de l'Inde et les perles d'Afrique,
Ton labeur de ce jour aurait eu moins de prix. (Strophe XXII)

………………………………………………

Le vrai Dieu, le Dieu fort est le Dieu des idées.
Sur nos fronts où le germe est jeté par le sort,
Répandons le Savoir en fécondes ondées ;
Puis, recueillant le fruit tel que de l'âme il sort,
Tout empreint du parfum des saintes solitudes,
Jetons l'œuvre à la mer, la mer des multitudes :
– *Dieu la prendra du doigt pour la conduire au port.* (Strophe XXVI)

According to Alfred de Vigny, God's sole interest is in the Idea. God is indifferent to the groans of the physical universe, but He will not let perish one single human thought.

Abstract

Scientific progress is in nature a permanent accumulation of experimental observations and data. However, pure accumulation is of limited value. A profound look behind the data is necessary to recognize relations between apparently remote observations and express these relations in universally valid concepts and models. Usually, such concepts are cornerstones for further scientific progress.

Based on the above premise and the experimental evidence that metallic iron (Fe^0) do remove more substances or substance classes from aqueous solutions than could be predicted for a reducing agent (Fe^0), the objective of the present work was to critically review the literature on “water treatment with Fe^0” and discuss the consequences for the further development of the technology of “using Fe^0 for water treatment”.

The first observation was that the approach to investigate processes in Fe^0/H_2O systems has been more pragmatic than systematic. In fact, iron walls have first been reported to effectively degrade solvents in groundwater. Subsequently, the ability of Fe^0 to treat other contaminants has been evaluated on a case-by-case basis. Quantitative removal of non-reducible species, oxidable species and species without redox properties has been reported as well. Therefore, the concept considering Fe^0 as a reducing agent has been questioned and proven inconsistent. A new concept has been introduced and validated which considers adsorption (and adsorptive size exclusion in column studies), and co-precipitation as fundamental contaminant removal mechanisms. Because removed contaminants are enmeshed in the matrix of transforming iron corrosion products, they are necessarily long-term stable under experimental and filed conditions. Thus, Fe^0 is a universal material for water treatment and in particular for safe drinking water production.

Next to the profound understanding of the mechanism of contaminant removal in packed Fe^0 beds, the volumetric expansive nature of iron oxidative dissolution at $pH > 4.5$ was properly considered. The result was the suggestion of Fe^0 volumetric proportions between 30 and 60 % for safe drinking water production at household level. Ideally, Fe^0 is mixed with porous inert materials which sustain the reactivity of Fe^0 by storing in-situ generated iron hydroxides.

The efficiency of a Fe^0 bed mostly depends on: (i) the intrinsic reactivity of used Fe^0, (ii) the thickness of the bed, and the water flow rate (or the residence time within the bed). Future experimental works should be focused on characterizing the intrinsic reactivity of potential affordable materials. It can be emphasized that Fe^0 beds will allow for the provision of household and remote small communities with safe drinking water.

Preface

The present work was presented as thesis for the Habilitation degree at the Faculty of Geoscience and Geography of the Georg-August-University of Göttingen for the achievement of the teaching licence (venia legendi) for Hydrogeochemistry and was accepted on November 09th 2010.

This thesis deals with the use of metallic iron (Fe^0) for water treatment in general and the use of Fe^0 for safe drinking water production in particular. The provision with safe drinking water is a real problem for 800 millions of people all over the world.

Chapter 1 presents the concept of water treatment with Fe^0 in a broader scientific context and reveals research needs. Chapter 2 presents the 21 peer-reviewed journal articles on which the thesis is based in relation to their contribution to solve the problems from Chapter 1. Chapter 3 presents the same articles in the perspective of using Fe^0 for safe drinking water production. Chapter 4 summarizes the major findings or the present work. An outlook is given in form of specific recommendations for future works. Chapter 5 gives an epilogue which is a sort of responses to the comments made by the referees on the submitted thesis. Chapter 6 lists cited references. The 21 papers on which this thesis is formulated are not appended to this version.

The experimental research was carried out at the Department of Applied Geology of the University of Göttingen (Prof. Martin Sauter) between July 2005 and March 2009 and partly was financed by the German Research Foundation (DFG) under the Grant number DFG NO 626/2-1 and DFG NO 626/2-2.

I would like to thank Angelina Schöner, Paul Waofo and Sabine Caré for the scientific collaboration during the study.

My acknowledgements also go to my colleagues of the Department of Applied Geology at the University of Göttingen, to my friends and collaborators for religious, cultural and sportive issues in Göttingen (and Krebeck), in Freiberg (Sachsen) and elsewhere. They provided the excellent atmosphere for this work.

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Contents

0 Introduction

0.1 Available technologies

The availability of clean drinking water is an universal problem faced both by developed and developing nations. Population growth has created a worldwide demand for new water sources. Many potential water sources contain high levels of contaminants from natural and anthropogenic origins that are hazardous to human health (WHO/UNICEF 2010). Natural contaminants include arsenic, uranium and pathogens (e.g. bacteria, viruses). Anthropogenic contaminants include dyes, pesticides and pharmaceuticals.

Whenever a water source is contaminated, it should be properly treated before release (e.g. wastewaters) or use (e.g. drinking water). Various technologies are available for water treatment at three levels: (i) drinking water production, (i) wastewater treatment, and (iii) environmental remediation. Pressures from financial, legislative and time-related constraints necessitate continued research into alternative techniques that provide better, faster and cheaper water treatment. Many conventional water treatment strategies are too expensive for extensive deployment in small municipalities and in the developing world (Coulibaly & Rodriguez 2004, Phillips 2009, Gottinger 2010). Therefore, affordable technologies using low cost materials and matching or exceeding the capability of conventional remediation technologies are needed.

For safe drinking water production, conventional treatments with coagulation, rapid sand filtration, granular activated carbon filtration, and disinfection (chlorination, ozonation or ultraviolet radiation) have been proven inefficient for the quantitative removal of several micro-pollutants from surface waters (Zhou & Smith 2002, Tansel 2008, Li et al. 2009, Srinivasan & Sorial 2009). Consequently, alternative and innovative water treatment concepts are under development (Tansel 2008, Li et al. 2009, Antia 2010, Tellen et al. 2010).

A new treatment four-stages-concept was recently proposed in the Netherlands: (i) fluidized ion exchange (FIEX), (ii) ultrafiltration (UF), (iii) nanofiltration (NF), (iv) granular activated carbon filtration (GAC) (Li et al. 2009). The FIEX process removes calcium and other divalent cations; the UF membrane removes particles and microorganisms; and the NF membrane and GAC remove natural organic matter (NOM) and micro-pollutants. The results of a pilot study showed successful removal of most micro-pollutants. However, very polar substances with a molecular weight lower than 100 Daltons could not be quantitative removed. These substances are too small to be rejected by the NF (size exclusion), and too polar to be quantitatively adsorbed by the GAC. Therefore, a process is needed to quantitatively remove both small and polar substances from water. Water filtration on metallic iron is a serious candidate as will be shown in this thesis.

The technology of using metallic iron (Fe^0) for safe drinking water production has been inspired by the 20 years old technology of iron reactive barriers. Water filtration using metallic iron will first be presented.

0.2 Water filtration on metallic iron

In early 1990, Fe^0 was introduced as reducing agent for groundwater remediation in permeable reactive barriers (iron walls). Fe^0 has been proven particularly efficient for the decontamination of halogenated organic compounds (O´Hannesin & Gillham 1998, Scherer et al. 2000, Henderson & Demond 2007). Subsequent studies have confirmed the efficiency of Fe^0 for quantitative removal of several substances (and substance classes) including nitrate, bromate, chlorate, nitro aromatics compounds, pathogens, pesticides, arsenic, chromium, copper, lead, triazoles, uranium, and zinc (Bigg & Judd 2000, Scherer et al. 2000, Henderson & Demond 2007, You et al. 2005, Diao & Yao 2009, Pradeep & Anshup 2009, Tellen et al. 2010). Although successful removal of reducible (e.g. Cr^{VI}, lindane) and non reducible (e.g. Zn^{II}, triazoles) contaminants has been reported, the initial premise of reductive transformation is still prevailing.

The unspecific nature of the processes yielding aqueous contaminant removal by Fe^0 is confirmed by reports on successful removal of more than 20 different species (including bacteria and viruses) in Fe^0-based filters (3-Kolshi and SONO filters) designed for arsenic removal at the household level in South East Asia (Hussam & Munir 2007, Tuladhar & Smith 2009). The qualitative aspect of the efficiency of Fe^0 materials for contaminant removal in iron walls and household filters is the motivation for this work. The most important output is that Fe^0 is an efficient filter material, allowing for the quantitative removal of all contaminants, including small size and polar species difficult to be eliminated in conventional water treatment plants. Contaminants are not removed by iron or individual corrosion products but by the whole process of iron corrosion.

The presentation will start with an overview on the Fe^0 remediation technology (Chapter 1). In this chapter the concept of water treatment with Fe^0 is presented in a broader scientific context and reveals research needs. Chapter 2 presents the appended articles in relation to their contribution to solve the problems from Chapter 1. Chapter 3 presents the appended articles in the perspective of using Fe^0 for safe drinking water production. Chapter 4 summarizes the major findings or the present work. An outlook is given in form of specific recommendations for future works. Chapter 5 lists cited references. The twenty one (21) peer-reviewed journal papers on which this thesis is formulated are listed in appendix.

1 Overview on the Fe^0 remediation technology

This chapter presents the technology of using metallic iron (Fe^0) for water treatment. The aim is not to give a complete review of almost 20 years intensive research. Comprehensive reviews on Fe^0 as remediation agent have been carried out recently (Tratnyek et al. 2003, Warner & Sorel 2003, Zhang 2003, Ebert 2004, Jambor et al. 2005, Li et al. 2006, Henderson & Demond 2007, Laine & Cheng 2007, Cundy et al. 2008, Thiruvenkatachari et al. 2008). The objective of the present work is to present a selection of key issues and questions which have not been properly addressed so far and which are essential for the further development of the technology.

1.1 Background

The idea of using geochemical barriers to mitigate contaminant migration in the environment as used in permeable reactive barriers (PRB) is not new (Artiole & Fuller 1979, Palmer and Wittbrodt 1991). The PRB technology for groundwater remediation was introduced in the 1990s as a passive alternative to active pump-and-treat remedial strategies (O’Hannesin & Gillham 1992, Starr & Cherry 1994). The PRB concept was introduced by McMurthy & Elton in 1985. The basic idea is to allow a polluted water to pass through an engineered structure containing a material that reacts with the contaminant to enhance its removal from the aqueous phase. The nature of the reactive material and the mechanism of contaminant removal depend on the nature of the contaminant (McMurthy & Elton 1985, Palmer & Wittbrodt 1991, Starr & Cherry 1994, Hamby 1996). Regardless of the removal mechanisms, PRB performance depends on: (i) appropriate placement of the barrier to capture the targeted contaminant plume, and (ii) sufficient residence time within the treatment wall to accomplish the desired removal goal. Conventionally, two treatment wall configurations are considered: the continuous barrier and the funnel and gate system (Starr & Cherry 1993, Starr & Cherry 1994, Painter 2005). Since the introduction of the PRB technology, numerous pilot tests, field tests, and commercial installations have been implemented (Muegge & Hadley 2009, Phillips et al. 2010). Most treatment walls have been constructed within the past few years (Jambor et al. 2005, Thiruvenkatachari et al. 2008). Recent estimates suggest that there are more than 200 currently operating PRBs around the world and applications of treatment wall technology will likely continue. The large majority of current full-scale treatment walls (approximately 120) uses Fe^0 as the reactive medium (Henderson & Demond 2007, Thiruvenkatachari et al. 2008).

1.2 Water remediation with Fe^0

Environmental remediation with Fe^0 was born as Reynolds et al. (1990) published their work on the potential of stainless steel and galvanized steel as casing materials used in groundwater monitoring wells to cause sampling bias for waters containing halogenated hydrocarbons. Their results showed in particular that trichloroethene is disappeared in the presence of stainless steel. This discovery coincided with the active seek of suitable reactive media for engineered walls according to the concept developed by McMurty & Elton (1985). Fe^0 materials are highly reactive, environmentally acceptable, and are readily available. They became the most promising reactive medium for engineered walls (Tratneyk et al. 2003, Jambor et al. 2005, Henderson & Demond 2007, Thiruvenkatachari et al. 2008). Within 20 years the iron wall technology has developed to a standard technology for groundwater remediation and wastewater treatment with worldwide acceptance (Henderson & Demond 2007, Johnson et al. 2008, Comba et al. 2011).

1.3 Current limitations

Despite its well-documented efficiency, the Fe^0 remediation currently has three major limitations (Lee et al. 2004, Mielczarski et al. 2005, Henderson & Demond 2007, Johnson et al. 2008, Jiao et al. 2009, Comba et al. 2011):

(i) the contaminant removal mechanisms are still not fully understood (Problem 1);

(ii) the longevity of the wall in terms of Fe^0 reactivity loss resulting from the build-up of mineral precipitates at the Fe^0 surface is not fully understood (Problem 2);

(iii) the longevity of the wall in terms of reduction in permeability resulting from the filling of hole rooms within the wall by mineral precipitates (Problem 3).

The importance of Problem 1 is currently underestimated as Fe^0 is considered a reducing agent for contaminants, only. However, Fe^0/H_2O systems have successfully removed non-reducible contaminants as well (Lai et al. 2006, Morrison et al. 2006). As concerning Problem 2 and Problem 3, Henderson & Demond (2007) reported Fe^0 reactivity loss is more likely to limit iron wall longevity than the reduction in permeability (permeability loss). While the problem of Fe^0 longevity is univocally recognized and is currently investigated, the mechanism of contaminant removal currently receives less attention (Lavine et al. 2001, Jiao et al. 2009). A proper understanding of the processes by which aqueous contaminants are removed in Fe^0/H_2O systems is very important and is significant for the system long-term reactivity of Fe^0 and the long-term stability of removed contaminants.

1.4 Classes of removed contaminants

There are several ways to differentiate contaminants: (i) chemical nature (e.g. degradable, ionic, organic, inorganic, radionuclides), and (ii) redox-reactivity (reducible, oxidable and non-sensitive). With respect to remediation with Fe^0, a fundamental difference exists between organic and inorganic contaminants (Ott 2000, Thiruvenkatachari et al. 2008). Organic contaminants can be broken down into innocuous elements (carbon, hydrogen, halogens, oxygen, sulphur, phosphorous, nitrogen) and compounds (mainly carbon dioxide and water). Conversely, most inorganic contaminants are themselves elements; they can not be destroyed but can only change speciation or be removed from the aqueous phase (or immobilized). Accordingly, remediation strategies must focus on transforming inorganic pollutants into forms that are non-toxic, not bioavailable, immobile, or capable of being removed from the subsurface. Moreover, the transformed (and parent) species should be removed from contaminated water.

1.5 Mechanisms of contaminant removal by Fe^0

1.5.1 Prevailing concept

Metallic iron is mostly regarded as an electron donor to degrade organic contaminants or to convert them into non-toxic or less toxic forms (e.g. reductive degradation, reductive precipitation). Accordingly, Fe^0 PRB is regarded as a reductive technology for organic contaminants (e.g. Laine & Cheng 2007, Thiruvenkatachari et al. 2008, Comba et al. 2011).

As regarding inorganic contaminants, reductive precipitation (Gu et al. 1998, Puls et al. 1999), co-precipitation (Lackovic et al. 2000, Komnitsas et al. 2006, Noubactep et al. 2006) and adsorption onto iron oxides and oxyhydroxides are considered as major reaction paths. Whether a contaminant is adsorbed, co-precipitated or reduced, it should not be remobilized under field conditions (Scherer et al. 2000). This prerequisite makes co-precipitation the most suitable removal mechanism as slowly precipitated iron oxides are not likely to be dissolved under natural conditions (Heron et al. 1994). In fact, pH changes could cause desorption of adsorbed contaminants. On the other hand, changes of the redox situation will cause contaminant re-oxidation. The reductive degradation/precipitation concept would not explain why some contaminants are oxidized in Fe^0/H_2O systems (Joo et al. 2004, Lee & Sedlak 2008). Oxidized contaminants are necessarily co-precipitated (Jiao et al. 2009, Ghauch et el. 2010a, Ghauch et el. 2010b). For example while investigating the process of diclofenac removal by Fe^0, Ghauch et el. (2010b) could identify both reduced and oxidized derivates of the parent chemical.

The identification of oxidative derivates and the removal of non- reducible species (e.g. Zn^{II}) in Fe^0/H_2O systems disqualify the concept regarding Fe^0 as a reducing agent. Moreover, while investigating the reductive dechlorination of carbon tetrachloride (CT) by Fe^0, Jiao et al. (2009) demonstrated that “*the adsorbed hydrogen atoms produced during the iron corrosion process are* *necessary for the dechlorination process of CT*." The results of Jiao et al. (2009) are particularly interesting because CCl_4 was one of the probe compounds used to demonstrate that contaminants are removed by chemical reduction (Matheson & Tratnyek 1994).

1.5.2 Revisited concept

The presentation above suggests that the role of the oxide scale on Fe^0 in the process of contaminant removal has not been properly addressed. Oxide scale formation on Fe^0 at $pH > 4.5$ is a fundamental characteristic of aqueous iron corrosion (Wilson 1923, Evans 1929, Stratmann & Müller 1994, Odziemkowski 2009). The universal oxide scale on Fe^0 has been regarded as inhibitory (curse) for aqueous contaminant removal in the presence of Fe^0.

The reductive transformation concept has never been univocally accepted (Warren et al. 1995, Lavine et al. 2001). For example, Warren et al. (1995) wrote, "a convincing mechanism for the reductive dehalogenation of haloorganics by zero-valence metals has not yet been proposed. Matheson & Tratnyek (1994) maintained that dehalogenation was not mediated by H_2(g) or Fe(II) in the bulk aqueous-phase solution, suggesting that observed reactions take place at the metal surface." Three years later, O'Hannesin & Gillham (1998) acknowledged, "there is a broad consensus that the process is an abiotic redox reaction involving reduction of the organic compound and oxidation of the metal". Despite this "broad consensus", the reductive transformation concept has felt to explain many experimental observations (e.g. Mantha et al. 2001, Lee et al. 2004, Mielczarski et al. 2005).

An alternative concept regarding the oxide scale on Fe^0 as beneficial (a blessing) for the process of aqueous contaminant removal has recently been introduced in the frame work of this thesis work (Noubactep 2007, Noubactep 2008, Noubactep 2010a). According to this concept contaminant are fundamentally adsorbed and co-precipitated within the mass of transforming corrosion products and are therefore stable under experimental conditions. This concept could explain all reported discrepancies (Noubactep 2007, Noubactep 2008).

Independent researchers could traceably demonstrate that quantitative contaminant removal is only observed when iron corrosion products are allowed to precipitate in the Fe^0/H_2O system (Ghauch & Tuqan 2009, Ghauch et al. 2010a, Ghauch et al. 2010b).

The view that adsorption and co-precipitation are the fundamental mechanisms of contaminant removal in Fe^0/H_2O systems suggests that Fe^0 is a universal medium for water treatment. Moreover, upon proper design, a Fe^0/H_2O bed will remove all contaminants by adsorptive size exclusion and co-precipitation (Chapter 2). This characteristic challenges the common assumption, that in view to differences in properties (adsorptivity, solubility, degradability), multiple contaminant mixtures may not efficiently be treated by a single material (e.g. Bayer & Finkel 2005, Pradeep & Anshup 2009). However, because contaminant removal in batch systems primarily depends on the affinity of contaminants to iron hydroxides (iron corrosion products), it is likely that species like Mo^{VI} with low adsorptive affinity to iron hydroxides are not quantitatively removed. In this case, a sequential treatment design will be necessary. The restrictive remark on batch systems is valid for system using injections of nano-scale Fe^0 (Noubactep & Caré 2010a,).

1.6 Applications of the new concept

The applications of the adsorption/co-precipitation concept are numerous and are a challenge for the research community. Strictly, a paradigm shift has occurred and the consequences for the development of the Fe^0 remediation technology are yet to be estimated. Two important aspects will be given below.

1.6.1 Designing Laboratory experiments

Two decades of intensive laboratory investigations have not elucidated the removal mechanism of aqueous contaminants in Fe^0/H_2O systems. Two of the major reasons for this are: (i) the failure to consider Fe^0/H_2O systems as consisted of Fe^0 covered by a layer of corrosion products, and (ii) the failure to treat properly the combined problem of mass transport and chemical reaction in these complex systems. Well-mixed batch experiments that have been undertaken in order to circumvent the mass-transport problem associated with bulk solutions have not always adequately addressed these key issues. Mixing intensity may not only affect the hydrodynamic but also the chemical dynamics, in particular the formation of the oxide-film. A critical review on the process of oxide scale formation and its impact on the process of mass-transport to the Fe^0 surface, have demonstrated that well-mixed batch systems are not an effective tool for investigating the mechanism of aqueous contaminant removal by Fe^0. In fact, any mixing operation (e.g. stirring, shaking) increases corrosion rate, delays the formation of the oxide scale, or provokes its abrasion. The critical review has let to the conclusions that quantitative contaminant removal occur within the oxide scale on Fe^0. Consequently: (i) non-shaken batch experiments are proposed as a simple tool to investigate mass-transport limitation through oxide-films at laboratory scale, (ii) experiments characterizing interactions in Fe^0/H_2O systems should be performed at low mixing intensities (e.g. < 50 rpm). Similarly, batch experiments should be performed with flow rates relevant to natural situations (Noubactep 2009a, Noubactep 2009b, Noubactep et al. 2009a, Noubactep et al. 2009b).

1.6.2 Designing iron beds

The pore surface diffusion model (PSDM) presented by Crittenden et al. (1986) for granular activated carbon (GAC) is currently used to model contaminant transport in Fe^0 beds (Arnold &

Roberts 2000, Bayer & Finkel 2005). The PSDM is a dynamic adsorption mass transfer model which incorporates (i) mass transfer by advective flow, (ii) liquid phase film transfer, (iii) pore and surface diffusion into the immobile liquid phase (intra-particle pores), and (iv) local equilibrium adsorption. The single modification that was rather optionally made was to simulate the development of oxide coatings or the reduction of the reactive Fe^0 surface over the total operation time (Bayer & Finkel 2005).

The presentation above has shown that no equilibrium state will be achieved in the presence of Fe^0 as iron corrosion is a continuous process. Furthermore, Fe^0 is not porous and its surface is not directly accessible to contaminants. Therefore, (i) the initial immobile phase (Fe^0) is reactive and (ii) pore and surface diffusion occur into the “new immobile phase” (corrosion products) which is in turn a transforming system. Accordingly, the original PSDM should be profoundly modified to take into account the dynamic nature of the system.

Another important feature of bed design will be discussed in Chapter 2. It deals with the proportion of Fe^0 and/or the nature of filling materials (reactivity and porosity). It can be anticipated that due to the expansive nature of iron corrosion (Caré et al. 2008), mixing Fe^0 with an inert material (gravel, rocks, sandstones) is a prerequisite for long-term reactivity and not as considered by O’Hannesin & Gillham (1998) a tool to save Fe^0 cost. In other words, economization of money is a positive side effect of proper system design. Calculations have shown that at least a volumetric proportion of 40 % (relative to a 100 % Fe^0) should be saved (Noubactep & Caré 2010b).

Finally, it should be highlighted that the very first reactive wall constructed at Borden (Ontario, Canada) for the demonstration of the feasibility of the new technology contained less that 10 vol-% (Fe^0) (O’Hannesin & Gillham 1998) and could never been clogged because the initial porosity of the system could not be filled by expansive iron corrosion products. In other words, because of insufficient system analysis, the Fe^0 reactive wall technology has been demonstrated on a very permeable system (10 vol-% Fe^0) but operating walls are necessarily less permeable (mostly 50 to 100 vol-% Fe^0).

2 Overview on the appended articles

2.1 Introduction

By 2002, the field of water treatment with metallic iron (Fe^0-based materials or Fe^0) had reached a threshold at which better organization becomes crucial for purposeful technology development (Tratnyek et al. 2003, Warner & Sorel 2003, Ebert 2004). For this innovative technology to meet its promises for science and society, a systematic organization was needed at several fronts. They include (i) elucidating the mechanism of contaminant removal, (ii) properly considering data from other research areas using Fe^0 in aqueous solution, (iii) assessing Fe^0 intrinsic reactivity, (iv) explaining available discrepancies, (v) rationalizing the selection of experimental protocols, (vi) rationalizing the validity of available models and concepts for predictive simulations.

The present work is a contribution to this effort. This chapter will summarize the achievements, which are presented in details in appended original articles and the next chapter will present these results in the perspective of using Fe^0 for safe drinking water production.

2.2 State-of-the-art

Using Fe^0 for water treatment is necessarily a multidisciplinary issue as iron corrosion (electrochemistry, metallurgy, physics) is used for aqueous contaminant removal (environmental chemistry, geochemistry, water chemistry). Accordingly, the state-of-the-art knowledge in all fields using Fe^0 in aqueous systems (Fe^0/H_2O systems) would have been considered from the beginning on. The state of the art is the highest level of development of a scientific field achieved at a particular time (www.wikipedia.org). A critical review of the literature on the remediation Fe^0/H_2O system revealed that data available in several areas of science are not properly considered (Noubactep 2007, Noubactep 2008, Noubactep 2010a): (i) aqueous iron corrosion (Noubactep & Schöner 2009, Noubactep & Schöner 2010a), (ii) corrosion in the petroleum industry (Noubactep & Schöner 2009), (iii) hydrometallurgy (Noubactep & Schöner 2009, Noubactep 2010b), and (iv) synthetic organic chemistry (Noubactep 2007). As a result, modern analytic techniques (e.g. McGuire et al. 2003) and sophisticated modelling tools (e.g. Bayer & Finkel 2005, Wang & Savage 2005) were used to investigate and simulate the Fe^0/H_2O system while considering Fe^0 as a reducing agent and completely ignoring some key process occurring under environmental conditions (see Chapter 1). However, reductive transformations are not the goal of remediation. Remediation or mitigation basically means contaminant removal. Accordingly, even reduced contaminants have to be removed from the aqueous phase. One should also remember that many reduction products are even more toxic that the parent compounds.

2.3 Mechanism of contaminant removal in Fe^0/H_2O systems

The presentation above has belittled the importance of contaminant reduction in Fe^0/H_2O systems. An example will be given for clarity. If an aqueous solution contains 10 mM of a chlorinated aliphatic hydrocarbon (e.g. $C_2H_4Cl_2$), completely reducing $C_2H_4Cl_2$ to C_2H_6 will yield 10 mM C_2H_6 which has to be removed below a threshold value before the water is regarded as treated. Fortunately, reducible (CCl_4, Cr^{VI}) and non-reducible (e.g. Zn^{II}) contaminants are quantitatively removed in Fe^0 beds (Morrison et al. 2002, Lai et al. 2006, Johnson et al. 2008, Noubactep et al. 2010). This strong argument and other considerations have yielded to the revision of the still prevailing view, that Fe^0 is a (strong) reducing agent for contaminant reductive transformation (Noubactep 2007, Noubactep 2008, Noubactep 2010a, Noubactep et al. 2010a).

The new concept considers that contaminants are adsorbed and enmeshed in the matrix of iron corrosion products. Accordingly, contaminants are progressively incorporated in the growing oxide film at the surface of Fe^0. The dynamic process of iron corrosion necessarily removes contaminant by a non specific mechanism. Removed contaminants could be further transformed (oxidized or reduced). Moreover, iron is corroded by water and trace amounts of contaminants and other solutes may impact the process by influencing the protectiveness of the oxide-film on Fe^0 (Nesic 2007, Noubactep 2009c). Consequently, assuring long-term reactivity of Fe^0 is the only way to render Fe^0/H_2O sustainable.

This logical deduction coupled to the expansive nature of iron corrosion has yielded to the conclusion that iron beds with more that 50 vol-% Fe^0 should be regarded as pure material wastage (Noubactep & Caré 2010b). In fact, calculations have shown that a 100 % Fe^0 bed will loss its permeability (porosity = 0) when only 51 vol-% of Fe^0 is consumed. Accordingly, mixing Fe^0 with an inert material is not a tool to save Fe^0 cost (e.g. O’Hannesin & Gillham 1998) but a prerequisite for a long-term reactivity (Noubactep & Caré 2010b). The statement is illustrated the best by very efficient Fe^0-based arsenic filters (e.g. 3-Kolshi filters) in South East Asia which were abandoned for non-sustainability (Hussam 2009). The technology could be re-vive by a simple replacement of the thin 100 % Fe^0 layer by thicker layers of Fe^0/additive in adequate proportions (e.g. 50:50 volumetric ratio for a Fe^0/quartz filter). This last point suggests that the selection of operational conditions is crucial for the sustainability of Fe^0/H_2O systems (Noubactep et al. 2009c, Noubactep & Schöner 2010b).

2.4 Importance of adequate operational conditions

Presently, there is no standard procedure for conducting experiments regarding the characterization of contaminant removal in Fe^0/H_2O systems. Various experimental procedures are employed by researchers. Employed procedures differ for instance in Fe^0 intrinsic reactivity, pH value, Fe^0 pre-treatment (e.g. acid wash), particle size (nm, µm, mm) and surface area, Fe^0 surface state, volume of used experimental vessels, nature and concentration of contaminants, buffer application, experimental duration, mixing operations (type and speed) (Noubactep 2009a, Noubactep 2009b, Noubactep et al. 2009a, Noubactep et al. 2009b, Noubactep 2010c). A critical consideration of the impact of individual operational parameters suggests that mixing operation was the most disturbing factor in characterizing Fe^0/H_2O systems (Noubactep 2009b, Noubactep et al. 2009a, Noubactep et al. 2009b). The pH value was identified as the most important parameter determining the reactivity of Fe^0 (Noubactep 2009a, Noubactep 2009b, Noubactep 2009c). The major output are that: (i) proprietary information on the Fe^0 manufacturing process (not accessible or non-available) is of great importance for the efficiency and sustainability of Fe^0 remediation systems; (ii) remediation with Fe^0 is limited to $pH > 5.0$; (iii) batch experiments should be performed under non-disturbed conditions or mixing conditions (shaking, stirring) still allowing the formation of an oxide-scale on Fe^0; (iv) and column experiments should be performed with flowing rate relevant for natural situations. Two tests for the characterization of Fe^0 intrinsic reactivity are introduced. The first test characterizes iron dissolution in a 0.02 M EDTA solution (Noubactep 2009a, Noubactep et al. 2009a). The second test characterizes the extend of the delay of the discoloration of a 12 mg/L methylene blue solution by Fe^0 in the presence of well-characterized MnO_2 (Noubactep 2009d). Both tests are facile, cost-effective and do not involve any stringent reaction conditions. Hopefully, these tests will be routinely used to characterize Fe^0 together with elemental composition, surface area for instance.

2.5 Validity of models for Fe^0 reactivity

The presentation above (in particular § 1.3) has clearly demonstrated the need of a paradigm shift as the Fe^0 remediation technology has neglected several important factors inherent to aqueous iron corrosion (Noubactep 2009e, Noubactep 2009f, Noubactep 2009g). It is obvious that the validity of models developed on an inconsistent basis is questionable. Several models have been developed to improve predictive simulations of efficiency and sustainability of Fe^0/H_2O systems. The most used model is the specific reaction rate constants k_{SA} concept (Johnson et al. 1996).

The k_{SA}-model relies on the assumption that aqueous contaminant disappearance proceeds by kinetics (k_{obs}) that are first-order irrespective of contaminant concentration. Therefore, k_{obs} should be contaminant-characteristic. Because the rate of contaminant removal by Fe^0 appeared also to be first-order with respect to the available reaction sites on Fe^0 (specific surface area - SSA), Johnson et al. (1996) introduced k_{SA} (k_{obs}/SSA ratio) as a more general descriptor of Fe^0 reactivity. Therefore, k_{SA} is considered a more appropriate for remediation design calculations and other inter-system comparisons than k_{obs}.

The first problem with the k_{SA}-model is that it is contaminant-specific, while one-contaminant systems are rare in nature. Moreover, Fe^0 is mostly corroded by water. The second and most important problem of the k_{SA}-model is that it neglects the presence of iron corrosion products on the surface of Fe^0 (Noubactep 2008e). However, iron corrosion products are of larger surface area and stronger affinity to contaminants that the bare Fe^0 surface (Noubactep 2009c, Noubactep 2008e).

The validity of the k_{SA}-model is dependent on not only the intrinsic Fe^0 reactivity and Fe^0 pre-treatment, but also on the operational experimental conditions (used Fe^0 mass loading, mixing intensity, Fe^0 particle size, and initial pH value). Currently used experimental conditions are too different from each other for a useful comparison by means of the k_{SA}-model (Noubactep 2008e).

The idea behind the k_{SA}-model is that there may be common underlying mechanisms for reactions in Fe^0/H_2O systems that provide a confidence for a non-site-specific permeable reactive barrier design (McGeough et al. 2007). The view that contaminants are adsorbed and co-precipitated by a non-specific mechanism suggests that material selection and system dimensioning are the two most operation factors controlling the efficiency and the sustainability of remediation Fe^0/H_2O systems. Accordingly, the thickness of a wall depends on site-specific geochemical conditions (including contaminant concentration) and the Fe^0 intrinsic reactivity (Noubactep & Caré 2010b).

2.6 Lessons from the past

The presentation above has described the short history of the innovative technology of using Fe^0 for water remediation. The first reactive wall was constructed in 1994 (O’Hannesin & Gillham 1998) and the first household Fe^0-based filter, the 3-Kolshi system, tested in 1999 (Hussam 2009). The present study has revealed that the great potential of Fe^0 treatment is yet to be exploited, as the majority of works are conducted on a pragmatic basis. The net result is that controversial observations were made from various experimental protocols making any re-evaluation effort impossible (Noubactep et al. 2009a, Noubactep et al. 2010a). Provided that the new views are accepted and implemented by the majority, it will lead to a large scale changes in the scientific worldview on Fe^0 remediation. Recently the view that adsorption and co-precipitation are the fundamental mechanisms of the process of contaminant removal in Fe^0/H_2O has been validated and adopted by an independent research group (Ghauch et al. 2010a, Ghauch et al. 2010b). Despite some initial skeptic views (Elsner et al. 2007, Kang & Choi 2009), the concept is progressively properly referenced in the scientific literature (Baeza et al. 2008, Simon et al. 2008, Flury et al. 2009, Satapanajaru et al. 2009, Dickinson & Scott 2010, Dou et al. 2010, Gyliene et al. 2010, Kiser & Manning 2010, Zhu et al. 2010). For example Kiser & Manning (2010) wrote: “*… substantial evidence now suggests that Fe(II) is the predominant reducing agent generated during corrosion of metallic Fe (Noubactep 2007, Noubactep 2008).*” A second example is the work of Dou et al. 2010 in which 7 references from 42 are articles from the appended list.

It is not unusual for technologies that the know-why precedes the know-how (Schmuki 2002, Post & Votta 2005, Noubactep & Schöner 2010a). For example, Noubactep & Schöner (2010a) reiterated that the proper understanding of the complex chemical and physical processes involved in electrocoagulation using Fe^0 (Fe^0 EC) as sacrificial electrode is still incomplete. The electrocoagulation was patented by Dieterich in 1906 and Fe^0 EC has been commercially used for decades. As a rule, profound understandings of the know-why open new doors for technology development.

During the last 20 years, a huge volume of data has been produced while using Fe^0 for water treatment. The fact is that iron remediation is an efficient technology. There should be no more pro or contra discussion for Fe^0. Rather, the whole remediation community should work on the conversion of these data into knowledge. It is a blessing that the funding research groups of the Fe^0 remediation technology are still active. It will be easy for each group to reconsider his own results than for any outstanding to search through the literature for data to re-evaluate.

The next chapter will compile the author contribution for the development of the Fe^0 remediation technology in the perspective of using Fe^0 for safe drinking water production at household and community level (Noubactep et al. 2009c, Noubactep & Caré 2010b, Noubactep & Schöner 2010b, Noubactep et al. 2010c).

3 Metallic iron for safe water production at household level

3.1 Background

This chapter summarizes the content of the appended papers in the perspective of using metallic iron (Fe^0) for small water treatment installations in single-family houses. Producing safe drinking water at household level is a human need of universal relevance. The presentation will discriminate between the situation in the developed and the developing worlds for clarity.

3.1.1 Household level water treatment in the developed world

In the developed world, metallic contamination from old piping systems, residues from water disinfection, and the presence of so-called emerging contaminants (mostly residues from pharmaceutical products) are three examples justifying the increasing trend to use bottled waters or household filters. Filtered water may be stored in PET bottles of doubtful quality. In fact, recent studies have reported leaching of Sb from PET bottles into mineral water and citrus fruit juices (Hansen et al. 2010).

Still in the developed world, many conventional water treatment technologies are too costly for extensive deployment in small municipalities (Coulibaly & Rodriguez 2004, Coulibaly & Rodriguez 2003, Gottinger 2010). On the other hand, there is a new trend for single-standing detached one family houses. Detached houses are sometimes built in remote rural areas. The connection of their engineering systems with old pipe and electric lines could be prohibitively expensive. Even where centralized water supply is available, a growing number of homeowners are interested in treating water at household level. This gives them an opportunity to choose the quality of the water they are using. In other words, people are not satisfied with available water and they wish to control what they drink. Therefore, for the developed world, household water treatment technologies matching or exceeding the capability of conventional technologies are needed.

3.1.1 Household level water treatment in the developing world

In many rural and peri-urban communities in the developing world, most people do not have any access to treated water. Their natural waters (rivers, springs, wells) are potentially contaminated with pathogens and various imported manufactured substances including fertilizers, heavy metals, herbicides, insecticides, and pharmaceutics (Shannon et al. 2008, Sobsey et al. 2008, Litter et al. 2010, Tellen et al. 2010). Here, there is obviously a larger need for efficient but affordable technologies for safe drinking water. Affordable treatment devices should additionally be easy to use and maintain (Hussam & Munir 2007, Ngai et al. 2007, Tellen et al. 2010).

Currently there are more than 800 million people without access to safe drinking water in the world and experts agree on the sad fact that the Millennium ´Development Goals for water (to "halve by 2015 the proportion of people without sustainable access to safe drinking water" in 2000) will not be achieved (WHO/UNICEF 2010). Therefore, a potential efficient and affordable technology must be worldwide applicable. Metallic iron (Fe^0) which is universally available is a good candidate.

3.2 Suitability of Fe^0 for household filters

The last two decades have witnessed the establishment of Fe^0 as powerful environmental remediation materials (Scherer et al. 2000, Henderson & Demond 2007, Cundy et al. 2008, Comba et al. 2011). Until recently, it has been commonplace to consider that the mechanism of metallic iron remediation varies depending on the contaminant of interest (O'Hannesin & Gillham 1998, Scherer et al. 2000, Henderson & Demond 2007, Cundy et al. 2008, Comba et al. 2011). Following this premise, research over the past decade has demonstrated the efficacy of Fe^0 for the remediation of a wide range of contaminants, including chlorinated organics, dyes, pharmaceutical products, selected inorganic ions, a wide range of heavy metals, and radionuclides (Cantrell et al. 1995, Blowes et al. 2000, Morrison et al. 2002, Morrison et al. 2006, Ghauch et al. 2010a, Ghauch et al. 2010b). Thereby, the used approach was a pragmatic one as contaminant removal was tested on case-by-case basis. In other words, available results on aqueous contaminant removal by Fe^0 could be collectively regarded as demonstration of the universal efficiency of Fe^0 filters for safe drinking water production.

Beside adsorption and co-precipitation, size exclusion is the third fundamental removal path of contaminants in Fe^0 filters. Accordingly, Fe^0 is used to assist sand filtration and not to induce any chemical transformation of contaminants. The volumetric expansive process of iron corrosion and the adsorptive properties of in situ generated iron oxides are used to sustain the filtration efficiency (Noubactep 2010a, Noubactep & Caré 2010b, Noubactep et al. 2010b). In other words, in Fe^0 filters, Fe^0 is oxidized by H_2O and corrosion products are used as trap for contaminants, which could be chemically transformed. Depending on their nature and concentration, selected contaminants may inhibit or sustain the process of iron corrosion. For example, it is well-established that the incorporation of a cation into the structure of iron (oxyhydr)oxides alters the nucleation, crystal growth, and transformation (Mitsunobu et al. 2010).

3.3 Mechanism of contaminant removal in Fe^0 filters

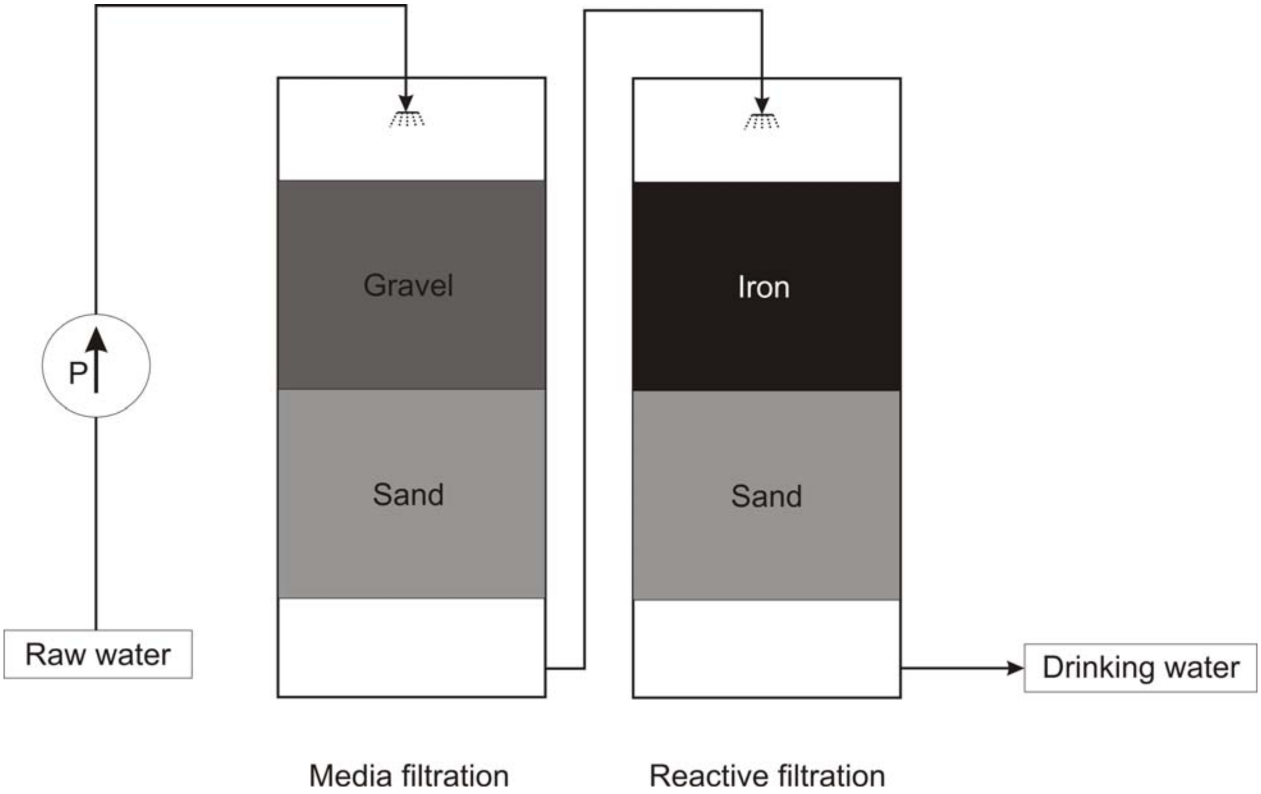

Figure 1: Flow scheme of treatment concept. Potential materials are enumerated without care on their relative proportions. In the reactive filtration bed, sand and iron particles are mixed. The volumetric proportion of Fe^0 should not exceed 50%.

3.3.1 Bed porosity and porosity loss

A Fe^0 filtration bed is composed of one or several reactive zones of granular sand and Fe^0 particles (Fig. 1). The compact Fe^0:sand mixture has a random porous structure. The manner with which the pore space is formed depends mainly on the arrangement of the granular particles (Nur et al. 1998). While packing uniform spheres, the least compact and most compact arrangements are rhombohedral and cubic respectively. The pore size can be defined in terms of a length dimension (pore radius). Pore size in a packed bed is closely related with the size of the filter grains constituting the bed (e.g. Fe^0 and sand). The smaller the grains are, the smaller the pore size is.

The most important feature of Fe^0 filters is the evolution of the initial porosity with the extent of volumetric expansive Fe^0 corrosion (Noubactep et al. 2010b) and its consequence for the process of contaminant removal. It has been shown that if a filter contains less that 50 vol-% of Fe^0, no porosity loss will occur upon Fe^0 depletion. In all the cases, a progressive diminution of pore radius will be observed. Assuming a purposeful selection of Fe^0 and sand grain size and a relevant Fe^0 volumetric ratio in a filter, the processes yielding contaminant removal in Fe^0 beds are discussed below.

3.3.2 Mechanism of contaminant removal in Fe^0 filters

In the conventional granular bed filtration (adsorptive filtration), contaminants have to be transported in the vicinity of the filter grains (e.g. activated carbon, metal oxide) by different transport mechanisms and then adhered to the grain surfaces by various attachment mechanisms for their successful removal (Manandhar & Vigneswaran 1991). Filtration is thus a complex process involving physico-chemical mechanisms and essentially depending on four major various factors: (i) filtration rate, (ii) media grain size, (iii) affinity of contaminant to bed media, and (iv) contaminant concentration. Depending on the media grain size and the size of the contaminant, a filtration bed may work as pure sieve (size exclusion). Size exclusion is used for example in rapid sand filtration for water clarification.

3.3.2.1 Adsorptive filtration and reactive filtration

Conventional filters contains adsorptive media (e.g. iron oxides), which are relatively inert in water and possess a given adsorptive capacity for any contaminant. Accordingly, a contaminant breakthrough is observed when the adsorptive capacity of the material in the filter is exhausted. In a Fe^0/sand bed, on the contrary, iron oxides for contaminant adsorption are generated in-situ. Ideally, iron oxide generation through Fe^0 oxidation H_2O (or H^+) occurs uniformly in the whole bed (Fig. 2). Therefore, although a reaction front exists due to dissolve O_2, salinity and probably contamination, virgin Fe^0 can not be expected in a Fe^0 filter (reactive filtration). Accordingly, at any date contaminant removal occurs in the whole bed and iron corrosion proceeds in all three compartments of the bed. The best illustration for this is given by an experiment of Leupin & Hug (2005). The authors performed an As removal experiment with four identical filters in series containing each 1.5 g Fe^0 and 60 g sand.

The results showed that 36 L of water containing 500 μg As/L could be treated to below 50 μg/L arsenic. This performance resulted from multiple filtrations, showing that contaminant removal occurs in the whole bed. The difference between synthetic iron oxides and in-situ generated iron oxides (corrosion products) is excellently given by Sikora & Macdonald (2000), and presented elsewhere in the context of safe drinking water production (Noubactep et al. 2009c). The further presentation will insist on the transformation of iron from its position in the metal lattice (Fe^0) to its location in a crystallized corrosion products (e.g. FeOOH, Fe_2O_3, Fe_3O_4).

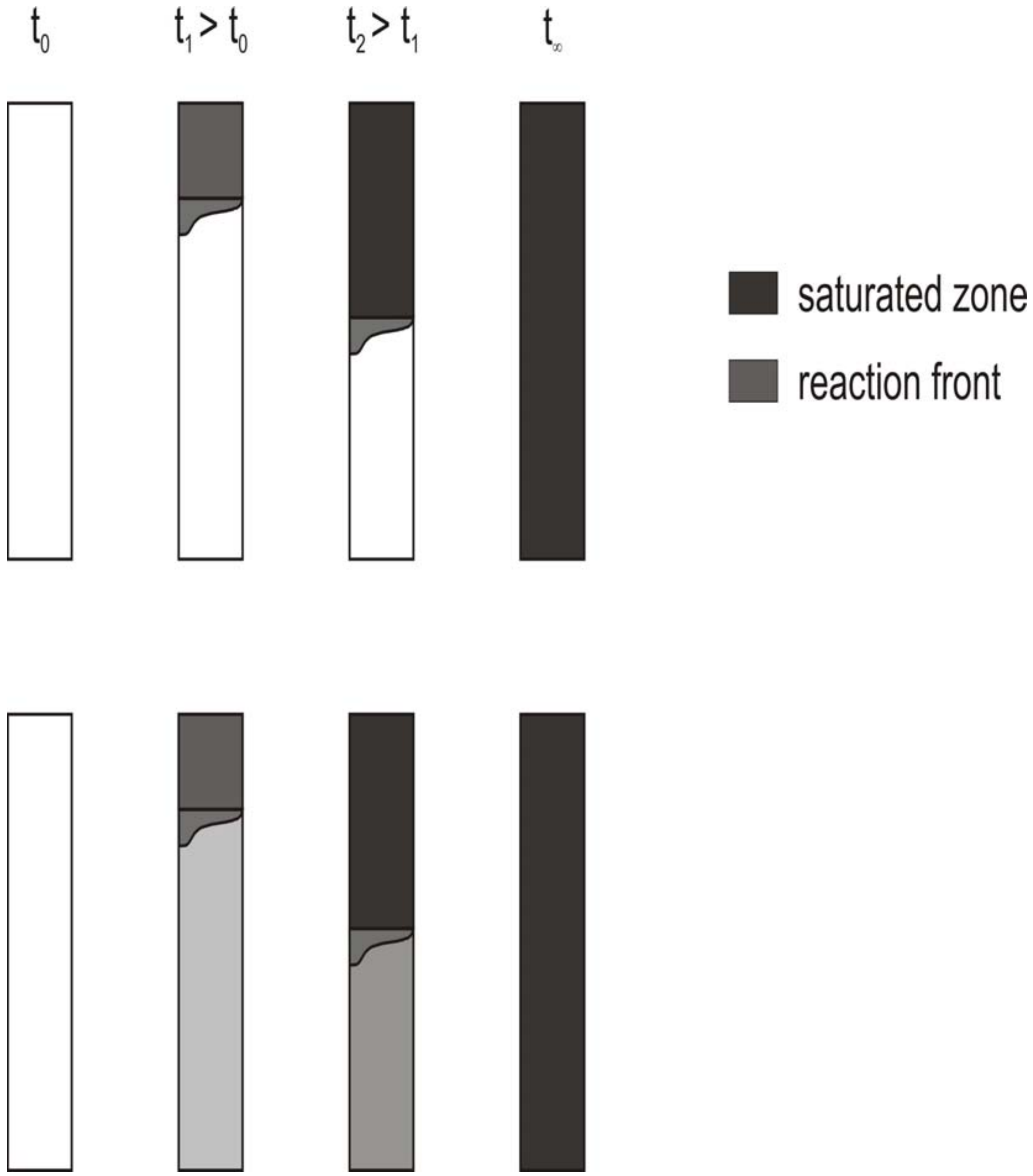

Figure 2: Comparison of the evolution of contaminant loading in granular activated carbon (GAC - up) and Fe^0 (dawn) filters. The evolution of the GAC filters is virgin - preloaded (reaction front) and saturated carbon. For the Fe^0 filters a reaction front may exist due to increased O_2 in the influent but iron corrosion by H_2O (or H^+) occurs uniformly in the whole column. The light grey shadow indicates progressive Fe^0 corrosion by water.

3.3.2.2 The volumetric expansion/compression cycle

The essential characteristic of a Fe^0 filtration bed is the in-situ generation of very adsorptive iron hydroxides which are progressively transformed to amorphous and crystalline iron oxides. While filling the pore space, solid corrosion products necessarily reduce the pore radius, improving size exclusion but the most important feature is the dynamic nature of iron corrosion in the pore space (Noubactep et al. 2009c, Noubactep 2010a, Noubactep 2010d, Noubactep 2010e, Noubactep et al. 2010b). Iron corrosion products could be regarded as “mercenaries” with the mission to trap contaminants in the pore space of the bed. Accordingly, contaminants do not need to be transported near the Fe^0 grains to be removed.

The cycle of a single atom (Fe^0) in the process of iron corrosion can be given as follows:

$Fe^0 \Rightarrow Fe^{2+}/Fe^{3+}(H_2O)_6 \Rightarrow Fe^{2+}/Fe^{3+}(OH)_n \Rightarrow FeOOH \Rightarrow Fe_2O_3 \Rightarrow Fe_3O_4$ (1)

While only considering insoluble species the cycle is:

$Fe^0 \Rightarrow Fe(OH)_2/Fe(OH)_3 \Rightarrow FeOOH \Rightarrow Fe_2O_3 \Rightarrow Fe_3O_4$ (2)

The transformation can also be represented in terms of variation of the specific surface area (SSA in m^2/g). Selected representative values are given in parenthesis, $Fe_2(HO)_6$ stands for ferrihydrite (Hanna 2007).

Fe^0 (1) $\Rightarrow Fe_2(HO)_6$ (327) $\Rightarrow$ FeOOH (55) $\Rightarrow Fe_2O_3$ (11) $\Rightarrow Fe_3O_4$ (2) (3)

The last alternative to represent the transformation is in terms volumetric expansion relative to Fe^0 in the metal lattice. The coefficient of volumetric expansion given in parenthesis is equal to V_{oxide}/V_{Fe} (Caré et al. 2008). The following evolution is given:

Fe^0 (1) $\Rightarrow Fe_2(HO)_6$ (6.4) $\Rightarrow$ FeOOH (3.0) $\Rightarrow Fe_2O_3$ (2.2) $\Rightarrow Fe_3O_4$ (2.1) (4)

The evolution of the surface area, the density and the coefficient of volumetric expansion clearly show that dissolved Fe first experiences an expansion than a compression. Focusing the attention on the initial stage (Fe^0) and the final stage (FeOOH, Fe_2O_3 or Fe_3O_4) reveal an expansion, which is definitively the reason for porosity loss. However, the whole dynamic process of iron corrosion should be considered. In particular, if there is not enough space for volumetric expansion, iron corrosion will stop. Strictly the porosity will decrease to zero. This corresponds to permeability loss (or porosity loss). This is the very first argument against a 100 % Fe^0 reactive zone of 100 % Fe^0 filtration bed as used in the 3-Kolshi system (Khan et al. 2000, Hussam 2009). Therefore, Leupin et al. (2005) suggested the admixture of inert sand to Fe^0 as an efficient tool to ameliorate the efficiency of iron filters. Recent calculations (Noubactep & Caré 2010b, Noubactep et al. 2010b) suggested that a reactive zone with more that 60 vol-% Fe^0 should be regarded as pure material wastage because corrosion will stop because of lack of space to proceed. It is important to notice that mixing Fe^0 and inert materials (e.g. sand) is a prerequisite for long-term Fe^0 reactivity (and filter permeability). Accordingly, the resulting economy in investment costs (costs for the corresponding up to 50 vol-% Fe^0) could be regarded as beneficial side effects.

3.3.2.3 Expansion/compression cycles and contaminant removal

The transformations accompanying Fe^0 transformation to crystallized iron oxides may occur in the presence of contaminants which may be trapped or enmeshed in the mass of corrosion products or be retained in the filter by size exclusion. The efficiency of a Fe^0 filter for contaminant removal can be summarized in the following metaphor: *Instead of waiting for the contaminants to come to its surface, Fe^0 injects corrosion products into the pore space for rapid and effective contaminant removal*. A further abstraction is to consider that the pore space is initially filled with porous amorphous iron hydroxides and oxides, which are progressively transformed to more crystalline species.

It is important to note that the presentation above has not considered the nature of the contaminants. Accordingly, even contaminants with less adsorptive affinity to iron oxides like Mo^{VI} (Morrison et al. 2002, 2006) will be transported in the filter by gravity, and removed by pure size exclusion. Specific laboratory researches are nevertheless needed for such contaminants. These studies may check the possibility to add a layer of adequate reactive materials (e.g. MnO_2 or natural zeolithe for Mo^{VI}) for the specific removal of such contaminants before or after Fe^0 filtration.

3.4. Filter design

Fe^0 filtration beds should remove trace amounts of chemical contaminants and pathogens from raw water to produce save drinking water. The filter efficiency depends upon the purposeful selection of a reactive medium (Fe^0) and the water flow velocity. The water flow velocity will depend on the intrinsic reactivity of Fe^0, as the residence time should correspond to the time necessary to produce enough iron corrosion for contaminant removal by (i) adsorption, (ii) co-precipitation and (iii) size exclusion.

It should be explicitly said that the goal should never be to select (or manufacture) the most reactive material but a material which is reactive enough to produce enough water for the community in need. For example, a Fe^0 material that is not reactive enough for a water plant in Germany could be satisfactorily for a plant in a tropical country (e.g. Cameroon). Nevertheless, having readily reactive materials has the advantage to offer flexibility in selecting the amount to be used in individual cases. For example, only 35 vol-% of a very reactive material could be used under tropical conditions and up to 60 vol-% under temperate conditions. Varying the reactivity of Fe^0 materials by varying their particle size from fine powders to large granules and chips will be a tool in optimising filtration efficiency.

A water treatment plant based on Fe^0 bed filtration is very simple and similar to slow sand filtration for small communities. The simplest device is a single column containing layers of: (i) gravel and sand for water clarification (media filtration) and (ii) Fe^0:sand for water treatment (reactive filtration). This device is similar to household Fe^0-based SONO filters (Hussam & Munir 2007, Hussam 2009) which have been reported to function for more than five years. The long-term efficiency of SONO filters is certainly due to the porous nature of the used composite.

3.5 The economics of Fe^0/sand beds

Cost is a major factor in implementing Fe^0 filtration technologies and is necessarily site-specific. Factors determining water treatment cost in Fe^0 beds include: (i) the quality of freshwater, (ii) plant or filter capacity, and (iii) construction costs. The realistic costs of Fe^0/sand filters given by Gottinger (2010) could be adopted here. The estimation is based on the evidence Fe^0 is the sole material to be bought. In Canada, Fe^0 filings can currently be obtained for under \$1.50 / kg (1.12 €/kg). The cost of manufacturing Fe^0/sand filter is comparable to a biological activated carbon filter. The service life of a Fe^0/sand filter (50 vol-% Fe^0) was estimated to be approximately 40 months (3.3 years). This yield to a treatment cost of < 0.01 \$/L (< 0.01 €/L) and includes filter installation, media, operation and maintenance costs. It is not likely that any water treatment could be cheaper than the own presented here.

3.6 Concluding remarks

Fe^0/sand filtration is an affordable technology for safe drinking water production at various scales: household, rural establishments (clinics, forestry stations, hospitals, hotels, schools), and small or large communities. Fe^0/sand filtration is the ideal technology for remote villages in the developing world (Noubactep & Schöner 2010b). Here inhabitants may lack money to purchase Fe^0 (no income) but they possess the ancestral iron-making technology (Pole 1982, Prakash 1991). It could be anticipated that, self produced safe drinking water will increase the self-confidence of rural populations and contribute to reduce rural exodus. On the other hand, the development and the implementation of the technology worldwide will render travel with bottle water superfluous. Moreover, Fe^0/sand filters are excellent candidates for safe drinking water in emergencies (e.g. earthquakes, wars, and tsunami).

Fe^0/sand filtration is equally a feasible option to successfully remove all target compounds from surface and groundwater: particles, natural organic matter, pathogens and micro-pollutants (including so-called emerging contaminants). Therefore, efforts should be made to use this chemical-free technology as the first choice everywhere. It could be expected that using Fe^0/sand filtration as standard technology will be very beneficial for water works as iron oxides (the products of iron corrosion) are easy to recycle to Fe^0. Recycling unit can be built within the facilities. The calcination of enmeshed organic contaminants will care for a porous recycled material. Porous Fe^0 materials are known for their increased reactivity. Possible enmeshed toxic inorganic substances are not likely to be leached out of the filters because or the low solubility of iron under working conditions (pH > 4.5).

The probably strongest argument for the development of Fe^0/sand filtration technology is the simplicity of the system. One should not care in parallel for membranes, granular activated carbon and chemicals (including disinfectants) but only on the stock of iron and sand, and the regeneration of the former. Finally, it can be speculated the success of the Fe^0/sand technology for safe drinking water production will depend on the capacity of researchers create new reactive Fe^0 materials and their capacity to find ways to control material reactivity in an affordable way.

4 Conclusions and outlook

Metallic iron remediation technology is being developed on a wrong basis while ignoring basic results from several research branches using Fe^0 in aqueous solutions. A critical system analysis is also missed. As a result, an inconsistent approach is available for: (i) system design, (ii) result interpretation, and (iii) predictive modelling. The present work has suggested a basic structure for a comprehensive system design. The introduced structure requires further study at several fronts to verify its overall usefulness.

4.1 System design

Experimental procedures reported over the last 20 years for the characterization of the process of aqueous contaminant removal by Fe^0 have been critically reviewed in terms of sample handling and appropriateness to simulate environmental situations. The results have clearly shown that available results are hardly comparable, as they have been achieved under very different experimental conditions (Noubactep et al. 2009a). A unified experimental procedure (e.g. standard procedure) for the investigation of processes in Fe^0/H_2O systems is suitable. A parameter (k_{EDTA} - Noubactep et al. 2009a) is introduced which could be routinely used to characterize Fe^0 reactivity under given experimental conditions. Furthermore, it is suggested that future batch experiments are only performed under mixing conditions still enabling the formation of an oxide scale near Fe^0. For column experiments, only flow rates relevant for natural situations will be used. Additionally no 100 % Fe^0 beds should be used, but rather, systems containing Fe^0 and inert materials. The Fe^0 volumetric proportion should not exceed 60 % (Noubactep & Caré 2010b, Noubactep et al. 2010b).

4.2 Result interpretation

The prevailing concept considers Fe^0 as a reducing agent. It is assumed that Fe^0/H_2O systems may remove chlorinated organics by reductive degradation, whereas metals, metalloids and radionuclides may be removed via reductive precipitation, surface adsorption or complexation, or co-precipitation with the Fe oxyhydroxides that are generated in the system (Scherer et al. 2000, Henderson & Demond 2007, Cundy et al. 2008). The validity of this concept is questioned in this work (Noubactep 2007, Noubactep 2008, Noubactep 2010a, Noubactep 2010d, Noubactep 2010e). In fact, given the large array of removed contaminants, some processes must be fundamental and valid for all possible pollutants while others will be valid only in particular situations (e.g., the contaminant is reducible). In addition to the diversity of successfully removed contaminants in Fe^0/H_2O systems, there is diversity among Fe^0 sources (intrinsic properties) and thus diversity in the chemical reactivity of used materials. The new concept was validated by own experimental results on methylene blue discoloration (Noubactep 2009a) and verified by the research group of Prof. Ghauch (Ghauch et al. 2010a, Ghauch et al. 2010b).

It is very important to notice that contaminant removal is caused by the whole dynamic process of aqueous iron corrosion (yielding adsorption and co-precipitation) rather than by Fe^0 strictly as a contaminant-removing agent. In Fe^0 beds, adsorptive size exclusion sustains the process of the contaminant removal. This is the rational behind using Fe^0 for safe water treatment (Noubactep & Caré 2010b, Noubactep & Schöner 2010b). On the other hand, the suitability of the injection of nano-scale Fe^0 for in-situ remediation of contaminated source is questioned (Noubactep & Caré 2010a).

4.3 Predictive modelling

In spite of the great number of models proposed to understand the processes occurring in a Fe^0/H_2O systems (e.g. Bayer & Finkel 2005, Wang & Savage 2005, Li et al. 2006, Beak & Wilkin 2009, Cong et al. 2010, Jeen et al. 2011), it is fair to say that none of them has the potential to be applied to real systems. In fact, they are all based on the premise that Fe^0 is a reducing agent, only. New modelling tools based on the view that the dynamic nature of iron corrosion is responsible for bed efficiency are yet to be developed. It is important to notice that contaminant removal on Fe^0 beds is neither an adsorptive nor a reactive filtration, which are characterized by a reaction front, but rather a bed filtration (Noubactep & Schöner 2010b). Therefore, the first tool to improve the Fe^0 bed efficiency is to thicken the reactive zone and mix Fe^0 with non-reactive materials (Noubactep & Caré 2010b, Noubactep et al. 2010b). On the other hand, regarding Fe^0 beds as "Fe^0 amended sand filters" (Noubactep 2010e) suggests that population balance models that account for pore and particle size distributions along with pore space topology (e.g. Bedrikovetsky 2008) describe processes in dynamic Fe^0/H_2O systems with better accuracy than currently used models (Jeen et al. 2011).

In summary, the present work should be regarded as a comprehensive evaluation of the process of aqueous contaminant removal using Fe^0. It offers a platform on which future works must be based for rapid technology development. A concerted effort within the scientific community is necessary to improve the efficiency of this cost effective remediation technology.

5 Epilogue

The presented work corresponds to the original manuscript evaluated by three anonymous referees. Minor revisions were performed, mostly limited at actualizing bibliographic references. The major concern of two referees was about the mechanism of organic contaminant removal in Fe^0/H_2O systems and is not addressed here for two reasons:

(i) the view that organic contaminants are removed by a different mechanism is not acceptable as has already been demonstrated in several reviews and comments (Noubactep 2011a). For an independent view see for example a recent work of Eusterhues et al. (2011) entitled "*Fractionation of organic matter due to reaction with ferrihydrite: Coprecipitation versus adsorption*".

(ii) the similarity between contaminant removal in metal/H_2O systems and electrocoagulation has been well-established (Bojic et al. 2004, 2007, 2009, Noubactep & Schöner 2010a). In particular, Bojic et al. (2009) stated that the mechanism of action of micro-alloyed aluminium is "*based on the several physico-chemical processes and the in situ formation of the coagulant, due to its spontaneous reaction with water. The major processes are adsorption, reduction, hydrogenation, hydrolysis and coagulation, operating synergistically to degrade and remove variety of pollutants from water, similarly as in process of electrocoagulation.*" They further wrote that "*the aluminium hydroxide flocks act as adsorbents and/or traps for ions, molecules or suspended particles thus removing them from the solution by sorption, co-precipitation or electrostatic attraction followed by coagulation."* This last statement corresponds to the major massage of two review articles by the author (Noubactep 2007, 2008).

Additionally, a more elaborated article was recently published (Noubactep 2010e) demonstrating more comprehensively how the synergy between adsorption, co-precipitation and adsorptive size-exclusion efficiently removes all aqueous contaminants in a well-designed Fe^0 bed.

Readers interested in testing the Fe^0 bed technology for save drinking water production are encouraged to use a recently published experimental design for column experiments (Noubactep & Caré 2011). In particular, mixing Fe^0 and contaminant release material (CRM) in long-term column experiments has the potential to accurately characterize of the suitability of Fe^0 materials for water treatment (Noubactep et al. 2005a, Noubactep 2011b). Appropriate three component systems "Fe^0 + reactive additive + CMR" can offer more investigation possibility. Two already positively tested reactive additive are FeS_2 and MnO_2 (Noubactep et al. 2003, Noubactep et al. 2005b, Ghauch et al. 2010a, 2010b).

6 Cited references

ANTIA D.D.J. (2010): Sustainable zero-valent metal (ZVM) water treatment associated with diffusion, infiltration, abstraction and recirculation. Sustainability 2, 2988–3073.

ARNOLD W.A. & ROBERTS A.L. (2000): Inter- and intraspecies competitive effects in reactions of chlorinated ethylenes with zero-valent iron in column reactors. Environ. Eng. Sci. 17, 291–302.

ARTIOLE J. & FULLER W.H. (1979): Effect of Crushed Limestone Barriers on Chromium Attenuation in Soils. J. Environ. Qual. 8, 503–510.

BAEZA A., SALAS A. & LEGARDA F. (2008): Determining factors in the elimination of uranium and radium from groundwaters during a standard potabilization process. Sci. Tot. Environ. 406, 24–34.

BAYER P. & FINKEL M. (2005): Modelling of sequential groundwater treatment with zero valent iron and granular activated carbon. J. Contam. Hydrol. 78, 129–146.

BEAK D.G. & WILKIN R.T. (2009): Performance of a zerovalent iron reactive barrier for the treatment of arsenic in groundwater: Part 2. Geochemical modelling and solid phase studies. J. Contam. Hydrol. 106, 15–28.

BEDRIKOVETSKY P. (2008): Upscaling of stochastic micro model for suspension transport in porous media. Transp. Porous Med.75, 335–369.

BIGG T. & JUDD S.J. (2000): Zero-valent iron for water treatment. Environ. Technol. 21, 661–670.

BLOWES D.W., PTACEK C.J., BENNER S.G., MCRAE CHE W.T., BENNETT T.A. & PULS R.W. (2000): Treatment of inorganic contaminants using permeable reactive barriers. J. Contam. Hydrol. 45, 123–137.

BOJIC A., PURENOVIC M., KOCIC B., PEROVIC J., URSIC-JANKOVIC J. & BOJIC D. (2001): The inactivation of escherichia coli by microalloyed aluminium based composite. FACTA UNIVERSITATIS, Phys. Chem. Technol. 2, 115–124.

BOJIC A., PURENOVIC M. & BOJIC D. (2004): Removal of chromium(VI) from water by micro-alloyed aluminium based composite in flow conditions. Water SA 30, 353–359.

BOJIC A.LJ., PURENOVIC M., BOJIC D. & ANDJELKOVIC T. (2007): Dehalogenation of trihalomethanes by a micro-alloyed aluminium composite under flow conditions. Water SA 33, 297–304.

BOJIC A.LJ., BOJIC D. & ANDJELKOVIC T. (2009): Removal of Cu^{2+} and Zn^{2+} from model wastewaters by spontaneous reduction–coagulation process in flow conditions. J. Hazard. Mater. 168, 813–819.

CANTRELL K.J., KAPLAN D.I. & WIETSMA T.W. (1995): Zero-valent iron for the in situ remediation of selected metals in groundwater. J. Hazard. Mater. 42, 201–212.

CARÉ S., NGUYEN Q.T., L'HOSTIS V. & BERTHAUD Y. (2008): Mechanical properties of the rust layer induced by impressed current method in reinforced mortar. Cement Concrete Res. 38, 1079–1091.

COMBA S., DI MOLFETTA A. & SETHI R. (2011): A Comparison between field applications of nano-, micro-, and millimetric zero-valent iron for the remediation of contaminated aquifers. Water Air Soil Pollut. 215, 595–607.

CONG X., XUE N., WANG S., LI K. & LI F. (2010): Reductive dechlorination of organochlorine pesticides in soils from an abandoned manufacturing facility by zero-valent iron. Sci. Tot. Environ. 408, 3418–3423.

COULIBALY H.D. & RODRIGUEZ M.J. (2003): Portrait of Drinking Water Quality in Small Quebec Municipal Utilities. Water Qual. Res. J. Canada 38, 49–76.

COULIBALY H.D. & RODRIGUEZ M.J. (2004): Development of performance indicators for small Quebec drinking water utilities. J. Environ. Manag. 73, 243–255.

CRITTENDEN J.C., HUTZLER N.J., GEYER D.G., ORAVITZ J.L. & FRIEDMAN G. (1986): Transport of organic compounds with saturated groundwater flow: model development and parameter sensitivity. Water Resour. Res. 22, 271–284.

CUNDY A.B., HOPKINSON L. & WHITBY R.L.D. (2008): Use of iron-based technologies in contaminated land and groundwater remediation: A review. Sci. Tot. Environ. 400, 42–51.

DE VIGNY A. (1864) : Les destinées : La Bouteille à la mer. Available at : http://romantis.free.fr/vigny/html/destines.html (Access 2011/04/12).

DIAO M. & YAO M. (2009): Use of zero-valent iron nanoparticles in inactivating microbes, Water Res. 43, 5243–5251.

DICKINSON M. & SCOTT T.B. (2010): The application of zero-valent iron nanoparticles for the remediation of a uranium-contaminated waste effluent. J. Hazard. Mater. 178, 171–179.

DOU X., LI R., ZHAO B. & LIANG W. (2010): Arsenate removal from water by zero-valent iron/activated carbon galvanic couples. J. Hazard. Mater. 182, 108–114.

EBERT M. (2004): Elementares Eisen in permeablen reaktiven Barrieren zur in-situ Grundwassersanierung - Kenntnisstand nach zehn Jahren Technologieentwicklung. Habilitationsschrift, Christian-Albrechts-Universität Kiel (Germany).

ELSNER M., CWIERTNY D.M., ROBERTS A.L. & LOLLAR B.S. (2007): Response to Comment on “1,1,2,2-Tetrachloroethane Reactions with OH-, Cr(II), Granular Iron, and a Copper-Iron Bimetal: Insights from Product Formation and Associated Carbon Isotope Fractionation”. Environ. Sci. Technol. 41, 7949–7950.

EUSTERHUES K., RENNERT T., KNICKER H., KGEL-KNABNER I., TOTSCHE K.U. & SCHWERTMANN U. (2011): Fractionation of organic matter due to reaction with ferrihydrite: Coprecipitation versus adsorption. Environ. Sci. Technol. 45, 527–533.

EVANS U.R. (1929): The distribution and velocity of the corrosion of metals, J. Franklin Inst. 208, 45–58.

FLURY B., EGGENBERGER U. & MÄDER U. (2009): First results of operating and monitoring an innovative design of a permeable reactive barrier for the remediation of chromate contaminated groundwater. Appl. Geochem. 24, 687–696.

GHAUCH A., ASSI H.A. & BDEIR S. (2010b): Aqueous removal of diclofenac by plated elemental iron: bimetallic systems. J. Hazard. Mater. 182, 64–74.

GHAUCH A., ASSI H.A. & TUQAN A. (2010a): Investigating the mechanism of clofibric acid removal in Fe^0/H_2O systems. J. Hazard. Mater. 176, 48–55.

GHAUCH A. & TUQAN A. (2009): Reductive destruction and decontamination of aqueous solutions of chlorinated antimicrobial agent using bimetallic systems. J. Hazard. Mater. 164, 665–674.

GOTTINGER A.M. (2010): Chemical-free arsenic removal from potable water with a ZVI-amended biofilter. Master thesis, University of Regina (Saskatchewan, Canada), 90 pp.

GU B., LIANG LIYUAN, DICKEY M.J., YIN X. & DAI S. (1998): Reductive precipitation of uranium (VI) by zero-valent iron. Environ. Sci. Technol. 32, 3366–3373.

GYLIENE O., VENGRIS T., NIVINSKIENE O. & BINKIENE R. (2010): Decontamination of solutions containing Cu(II) and ligands tartrate, glycine and quadrol using metallic iron. J. Hazard. Mater. 175, 452–459.

HAMBY D.M. (1996): Site remediation techniques supporting environmental restoration activities – a review. Sci. Tot. Environ. 191, 203–224.

HANNA K. (2007): Sorption of two aromatic acids onto iron oxides: Experimental study and modelling. J. Colloid Interf. Sci. 309, 419–428.

HANSEN C., TSIRIGOTAKI A., BAK S.A., PERGANTIS S.A., STEURUP S., GAMMELGAARDA B. & HANSEN H.R. (2010): Elevated antimony concentrations in commercial juices. J. Environ. Monit., 12, 822–824.

HENDERSON A.D. & DEMOND A.H. (2007): Long-term performance of zero-valent iron permeable reactive barriers: a critical review. Environ. Eng. Sci. 24, 401–423.

HERON G., CROUZET C., BOURG C.M.A. & CHRISTENSEN H.T. (1994): Speciation of Fe(II) and Fe(III) in contamninated aquifer sediments using chemical extraction techniques. Environ. Sci. Technol. 28, 1698–1705.

HUSSAM A. (2009): Contending with a Development Disaster: SONO Filters Remove Arsenic from Well Water in Bangladesh. Innovations 4, 89–102.

HUSSAM A. & MUNIR A.K.M. (2007) A simple and effective arsenic filter based on composite iron matrix: Development and deployment studies for groundwater of Bangladesh. J. Environ. Sci. Health A 42, 1869–1878.

JAMBOR J.L. RAUDSEPP M. & MOUNTJOY K. (2005): Mineralogy of permeable reactive barriers for the attenuation of subsurface contaminants. Can. Miner. 43, 2117–2140.

JEEN S.-W., GILLHAM R.W. & PRZEPIORA A. (2011): Predictions of long-term performance of granular iron permeable reactive barriers: Field-scale evaluation. J. Contam. Hydrol. 123, 50–64.

JIAO Y., QIU C., HUANG L., WU K., MA H., CHEN S., MA L. & WU L. (2009): Reductive dechlorination of carbon tetrachloride by zero-valent iron and related iron corrosion. Appl. Catal. B: Environ. 91, 434–440.

JOHNSON R.L., THOMS R.B., JOHNSON R.O'B. & KRUG T. (2008): Field evidence for flow reduction through a zero-valent iron permeable reactive barrier. Ground Water Monit. Remed. 28, 47–55.

JOHNSON T.L., SCHERER M.M. & TRATNYEK P.G. (1996): Kinetics of halogenated organic compound degradation by iron metal. Environ. Sci. Technol. 30, 2634–2640.

JOO S.H., FEITZ A.J. & WAITE T.D. (2004): Oxidative degradation of the carbothioate herbicide, molinate, using nanoscale zero-valent iron. Environ. Sci. Technol. 38, 2242–2247.

KANG S.-H. & CHOI W. (2009): Response to Comment on “Oxidative Degradation of Organic Compounds Using Zero-Valent Iron in the Presence of Natural Organic Matter Serving as an Electron Shuttle”. Environ. Sci. Technol. 43, 3966–3967.

KHAN A.H., RASUL S.B., MUNIR A.K.M., HABIBUDDOWLA M., ALAUDDIN M., NEWAZ S.S. & HUSSAM A. (2000): Appraisal of a simple arsenic removal method for groundwater of bangladesh. J. Environ. Sci. Health, A35, 1021–1041.

KISER J.R. & MANNING B.A. (2010): Reduction and immobilization of chromium(VI) by iron(II)-treated faujasite. J. Hazard. Mater. 174, 167–174.

KOMNITSAS, K., G. BARTZAS & PASPALIARIS I. (2006). Inorganic contaminant fate assessment in zero-valent iron treatment walls. Environ. Forensics, 7, 207–217.

LACKOVIC J.A., NIKOLAIDIS N.P. & DOBBS G.M. (2000): Inorganic arsenic removal by zero-valent iron. Environ. Eng. Sci. 17, 29–39.

LAI K.C.K., LO I.M.C., BIRKELUND V. & KJELDSEN P. (2006): Field monitoring of a permeable reactive barrier for removal of chlorinated organics. J. Environ. Eng. 132, 199–210.

LAINE D.F. & CHENG I.F. (2007): The destruction of organic pollutants under mild reaction conditions: A review. Microchem. J. 85, 183–193.

LAVINE B.K., AUSLANDER G. & RITTER J. (2001): Polarographic studies of zero valent iron as a reductant for remediation of nitroaromatics in the environment, Microchem. J., 70, 69–83.

LEE C. & SEDLAK D.L. (2008): Enhanced formation of oxidants from bimetallic nickel-iron nanoparticles in the presence of oxygen. Environ. Sci. Technol. 42, 8528–8533.

LEE G., RHO S. & JAHNG D. (2004): Design considerations for groundwater remediation using reduced metals. Korean J. Chem. Eng. 21, 621–628.

LEUPIN O.X. & HUG S.J. (2005): Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron. Wat. Res. 39, 1729–740.

LEUPIN O.X., HUG S.J. & BADRUZZAMAN A.B.M. (2005): Arsenic removal from Bangladesh tube well water with filter columns containing zerovalent iron filings and sand. Environ. Sci. Technol. 39, 8032–8037.

LI L., BENSON C.H. & LAWSON E.M. (2006b): Modelling porosity reductions caused by mineral fouling in continuous-wall permeable reactive barriers. J. Contam. Hydrol. 83, 89–121.

LI X.-Q., ELLIOTT D.W. & ZHANG W.-X. (2006b): Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects. Crit. Rev. Solid State Mater. Sci. 31, 111–122.

LI S., HEIJMAN S.G.J., VERBERK J.Q.J.C. & VAN DIJK J.C. (2009): An innovative treatment concept for future drinking water production: fluidized ion exchange – ultrafiltration – nanofiltration – granular activated carbon filtration, Drink. Water Eng. Sci. 2, 41–47.

LITTER M.I., MORGADA M.E. & BUNDSCHUH J. (2010): Possible treatments for arsenic removal in Latin American waters for human consumption. Environ. Pollut. 158, 1105–1118.

MANANDHAR U.K. & VIGNESWARAN S. (1991): Effect of media size gradation and varying influent concentration in deep-bed filtration: Mathematical models and experiments. Sep. Technol. 1, 178–183.

MANTHA R., TAYLOR K.E., BISWAS N. & BEWTRA J.K. (2001): A continuous system for Fe^0 reduction of nitrobenzene in synthetic wastewater, Environ. Sci. Technol. 35, 3231–3236.

MATHESON L.J. & TRATNYEK P.G. (1994): Reductive dehalogenation of chlorinated methanes by iron metal. Environ. Sci. Technol. 28, 2045–2053.

McGeough K.L., KALIN R.M. & MYLES P. (2007): Carbon disulfide removal by zero valent iron. Environ. Sci. Technol. 41, 4607–4612.

MCGUIRE M.M., CARLSON D.L., VIKESLAND P.J., KOHN T., GRENIER A.C., LANGLEY L.A., ROBERTS A.L. & FAIRBROTHER D.H. (2003): Applications of surface analysis in the environmental sciences: dehalogenation of chlorocarbons with zero-valent iron and iron-containing mineral surfaces. Anal. Chim. Acta 496, 301–313.

McMurty D.C. & ELTON R.O. (1985): New approach to in situ treatment of contaminated groundwaters. Environ. Prog. 4, 168–70.

MIELCZARSKI J.A., ATENAS G.M. & MIELCZARSKI E. (2005): Role of iron surface oxidation layers in decomposition of azo-dye water pollutants in weak acidic solutions. Appl. Catal. B 56, 289–303.

MITSUNOBU S., TAKAHASHI Y., TERADA Y. & SAKATA M. (2010): Antimony(V) incorporation into synthetic ferrihydrite, goethite, and natural iron oxyhydroxides. Environ. Sci. Technol. 44, 3712–3718.

MORRISON S.J., METZLER D.R. & DWYER B.P. (2002): Removal of As, Mn, Mo, Se, U, V and Zn from groundwater by zero-valent iron in a passive treatment cell: reaction progress modelling. J. Contam. Hydrol. 56, 99–116.

MORRISON S.J., MUSHOVIC P.S. & NIESEN P.L. (2006): Early breakthrough of molybdenum and uranium in a permeable reactive barrier. Environ. Sci. Technol. 40, 2018–2024.

MORTON DEY W. (1936): The Pessimism and Optimism of Alfred de Vigny, Studies in Philology 33, 405-416.

MUEGGE J.P. & HADLEY P.W. (2009): An evaluation of permeable reactive barrier projects in California, Remediation 20, 41–57.

NESIC S. (2007): Key issues related to modelling of internal corrosion of oil and gas pipelines – A review. Corros. Sci. 49, 4308–4338.

NGAI T.K.K., SHRESTHA R.R., DANGOL B., MAHARJAN M. & MURCOTT S.E. (2007): Design for sustainable development—Household drinking water filter for arsenic and pathogen treatment in Nepal. J. Environ. Sci. Health A42, 1879–1888.

NOUBACTEP C. (2007): Processes of contaminant removal in "Fe^0–H_2O" systems revisited. The importance of co-precipitation. Open Environ. J. 1, 9–13.

NOUBACTEP C. (2008): A critical review on the mechanism of contaminant removal in Fe^0–H_2O systems. Environ. Technol. 29, 909–920.

NOUBACTEP C. (2009a): Characterizing the discoloration of methylene blue in Fe^0/H_2O systems. J. Hazard. Mater. 166, 79–87.

NOUBACTEP C. (2009b): Characterizing the effects of shaking intensity on the kinetics of metallic iron dissolution in EDTA. J. Hazard. Mater. 170, 1149–1155.

NOUBACTEP C. (2009c): An analysis of the evolution of reactive species in Fe^0/H_2O systems. J. Hazard. Mater. 168, 1626–1631.

NOUBACTEP C. (2009d): Characterizing the reactivity of metallic iron upon methylene blue discoloration in $Fe^0/MnO_2/H_2O$ systems. J. Hazard. Mater. 168, 1613–1616.

NOUBACTEP C. (2009e): On the validity of specific rate constants (k_{SA}) in Fe^0/H_2O systems. J. Hazard. Mater164, 835–837.

NOUBACTEP C. (2009f): On the operating mode of bimetallic systems for environmental remediation. J. Hazard. Mater. 164, 394–395.

NOUBACTEP C. (2009g): Metallic iron for environmental remediation: Learning from the Becher Process. J. Hazard. Mater. 168, 1609–1612.

NOUBACTEP C. (2010a): The suitability of metallic iron for environmental remediation. Environ. Progr. Sust. En. 29, 286–291.

NOUBACTEP C. (2010b): Elemental metals for environmental remediation: Learning from cementation process. J. Hazard. Mater. 181, 1170–1174.

NOUBACTEP C. (2010c): Characterizing the reactivity of metallic iron in $Fe^0/EDTA/H_2O$ systems with column experiments. Chem. Eng. J. 162, 656–661.

NOUBACTEP C. (2010d): The fundamental mechanism of aqueous contaminant removal by metallic iron. Water SA 36, 663–670.

NOUBACTEP C. (2010e): Metallic iron for safe drinking water worldwide. Chem. Eng. J. 165, 740–749.

NOUBACTEP C. (2011a): Comment on "Reductive dechlorination of g-hexachloro-cyclohexane using Fe-Pd bimetallic nanoparticles" by Nagpal et al. [J. Hazard. Mater. 175 (2010) 680-687]. J. Hazard. Mater., doi: 10.1016/j.jhazmat.2011.03.081.

NOUBACTEP C. (2011b): Characterizing the reactivity of metallic iron in $Fe^0/U^{VI}/H_2O$ systems by long-term column experiments. Chem. Eng. J., doi:10.1016/j.cej.2011.03.093.

NOUBACTEP C. & CARÉ S. (2010a): On nanoscale metallic iron for groundwater remediation. J. Hazard. Mater. 182, 923–927.

NOUBACTEP C. & CARÉ S. (2010b): Enhancing sustainability of household water filters by mixing metallic iron with porous materials. Chem. Eng. J. 162, 635–642.

NOUBACTEP C. & CARÉ S. (2011): Designing laboratory metallic iron columns for better result comparability. J. Hazard. Mater., doi: 10.1016/j.jhazmat.2011.03.016.

NOUBACTEP C., CARÉ S., TOGUE-KAMGA F., SCHÖNER A. & WOAFO P. (2010b): Extending service life of household water filters by mixing metallic iron with sand. Clean – Soil, Air, Water 38, 951–959.

NOUBACTEP C., KURTH A.-M.F. & SAUTER M. (2009b): Evaluation of the effects of shaking intensity on the process of methylene blue discoloration by metallic iron. J. Hazard. Mater. 169, 1005–1011.

NOUBACTEP C., LICHA T., SCOTT T.B., FALL M. & SAUTER M. (2009a): Exploring the influence of operational parameters on the reactivity of elemental iron materials. J. Hazard. Mater. 172, 943–951.

NOUBACTEP C., MEINRATH G., DIETRICH P., SAUTER M. & MERKEL B. (2005): Testing the suitability of zerovalent iron materials for reactive walls. Environ. Chem. 2, 71–76.

NOUBACTEP C., MEINRATH G. & MERKEL J.B. (2005): Investigating the mechanism of uranium removal by zerovalent iron materials. Environ. Chem. 2, 235–242.

NOUBACTEP C., MEINRATH G., DIETRICH P. & MERKEL B. (2003): Mitigating uranium in ground water: prospects and limitations. Environ. Sci. Technol. 37, 4304–4308.

NOUBACTEP C. & SCHÖNER A. (2010a): Metallic iron for environmental remediation: Learning from electrocoagulation. J. Hazard. Mater. 175, 1075–1080.

NOUBACTEP C. & SCHÖNER A. (2010b): Metallic iron: dawn of a new era of drinking water treatment research? Fresen. Environ. Bull. 19, 1661–1668.

NOUBACTEP C., SCHÖNER A. & MEINRATH G. (2006): Mechanism of uranium (VI) fixation by elemental iron. J. Hazard Mater. 132, 202–212.

NOUBACTEP C., SCHÖNER A. & SAUTER M. (2010a): Significance of oxide-film in discussing the mechanism of contaminant removal by elemental iron materials. In "Photo-Electrochemistry & Photo-Biology for the Sustainablity"; S. Kaneco, B. Viswanathan, H. Katsumata (Eds.), Bentham Science Publishers, 1, 34–55.

NOUBACTEP C., SCHÖNER A. & WOAFO P. (2009c): Metallic iron filters for universal access to safe drinking water. Clean 37, 930–937.

NOUBACTEP C. & SCHÖNER A. (2009): Fe^0-based alloys for environmental remediation: Thinking outside the box. J. Hazard. Mater. 165, 1210–1214.

NUR A., MAVKO G., DVORKIN J. & GALMUDI D. (1998): Critical porosity; a key to relating physical properties to porosity in rocks. The Leading Edge 17, 357–362.

O'HANNESIN S.F. & GILLHAM R.W. (1992): A permeable reaction wall for in situ degradation of halogenated organic compounds, Proc. 5th Canadian Geotechnical Society Conf., Toronto, Ontario and Canada, October 25-28.

ODZIEMKOWSKI M. (2009): Spectroscopic studies and reactions of corrosion products at surfaces and electrodes. Spectrosc. Prop. Inorg. Organomet. Compd. 40, 385–450.

O'HANNESIN S.F. & GILLHAM R.W. (1998): Long-Term Performance of an In Situ "Iron Wall" for Remediation of VOCs. Ground Water 36, 164–170.

OTT N. (2000): Permeable Reactive Barriers for Inorganics, USEPA,Washington, DC, Report obtained from website http://www.clu-in.org (Access 2010/05/25).

PAINTER B.D.M. (2005): Optimization of permeable reactive barriers for the remediation of contaminated groundwater. Dissertation, Lincoln University, New Zealand.

PALMER C.D. & WITTBRODT P.R. (1991): Processes affecting the remediation of chromium-contaminated sites. Environ. Health Perspect. 92, 25–40.

PHILLIPS D.H. (2009): Permeable reactive barriers: A sustainable technology for cleaning contaminated groundwater in developing countries. Desalination 248, 352–359

PHILLIPS D.H., VAN NOOTEN T., BASTIAENS L., RUSSELL M.I., DICKSON K., PLANT S., AHAD J.M.E., NEWTON T., ELLIOT T. & KALIN R.M. (2010): Ten year performance evaluation of a field-scale zero-valent iron permeable reactive barrier installed to remediate trichloroethene contaminated groundwater. Environ. Sci. Technol. 44, 3861–3869.

POLE L.M. (1982): Decline or survival? Iron production in West Africa from the seventeenth to the twentieth centuries. J. African Hist. 23, 503–513.

POST D.E. & VOTTA L.G. (2005): Computational science demands a new paradigm. Physics Today, January 2005, 35–41.

PRADEEP T. & ANSHUP (2009): Noble metal nanoparticles for water purification: A critical review, Thin Solid Films 517, 6441–6478.

PRAKASH B. (1991): Metallurgy of iron and steel making and blacksmithy in ancient India. Indian J. History Sci. 261, 351–371.

PULS R.W., PAUL C.J. & POWELL R.M. (1999): The application of in situ permeable reactive (zero valent iron) barrier technology for the remediation of chromate-contaminated groundwater: a field test. Appl. Geochem. 14, 989–1000.

REYNOLDS G.W., HOFF J.T. & GILLHAM R.W. (1990): Sampling bias caused by materials used to monitor halocarbons in groundwater. Environ. Sci. Technol. 24, 135–142.

ROOKER J.K. (1914): The optimism of Alfred de Vigny. The Modern Language Review 9, 1-11.

SATAPANAJARU T., ONANONG S., COMFORT S.D., SNOW D.D., CASSADA D.A. & HARRIS C. (2009): Remediating dinoseb-contaminated soil with zerovalent iron. J. Hazard. Mater. 168, 930–937.

SCHERER M.M., RICHTER S., VALENTINE R.L. & ALVAREZ P.J.J. (2000): Chemistry and microbiology of permeable reactive barriers for in situ groundwater clean up. Rev. Environ. Sci. Technol. 30, 363–411.

SCHMUKI P. (2002): From Bacon to barriers: a review on the passivity of metals and alloys. J. Solid State Electrochem. 6, 145–164.

SHANNON M.A., BOHN P.W., ELIMELECH M., GEORGIADIS J.G., MARINAS B.J. & MAYES A.M. (2008): Science and technology for water purification in the coming decades Nature 452, 301–310.

SIKORA E. & MACDONALD D.D. (2000): The Passivity of Iron in the Presence of Ethylenediaminetetraacetic Acid I. General Electrochemical Behavior. J. Electrochem. Soc. 147, 4087–4092.

SIMON F.G., BIERMANN V. & PEPLINSKI B. (2008): Uranium removal from groundwater using hydroxyapatite. Appl. Geochem. 23, 2137–2145.

SOBSEY M.D., STAUBER C.E., CASANOVA L.M., BROWN J.M. & ELLIOTT M.A. (2008): Point of use household drinking water filtration: A practical, effective solution for providing sustained access to safe drinking water in the developing world. Environ. Sci. Technol. 42, 4261–4267.

SRINIVASAN R. & SORIAL G.A. (2009): Treatment of perchlorate in drinking water: A critical review, Sep. Purif. Technol. 69, 7–21.

STARR R.C. & CHERRY J. (1993): Funnel and gate system directs plumes to in situ treatment. Ground Water Currents 1993, 1–4.

STARR R.C. & CHERRY J.A. (1994): In situ remediation of contaminated groundwater: the funnel-and-gate system. Ground Water 32, 465–476.

STRATMANN M. & MÜLLER J. (1994): The mechanism of the oxygen reduction on rust-covered metal substrates. Corros. Sci. 36, 327–359.

TANSEL B. (2008): New technologies for water and wastewater treatment: A survey of recent patents, Recent Pat. Chem. Eng. 1, 17–26.

TELLEN V., NKENG G. & DENTEL S. (2010): Improved filtration technology for pathogen reduction in rural water supplies. Water 2, 285–306.

THIRUVENKATACHARI R., VIGNESWARAN S. & NAIDU R. (2008): Permeable reactive barrier for groundwater remediation. J. Ind. Eng. Chem. 14, 145–156.

TRATNYEK, P.G., SCHERER, M.M., JOHNSON, T.J. & MATHESON, L.J. (2003): Permeable reactive barriers of iron and other zero-valent metals. In Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial Applications, Tarr, M.A., Ed., Marcel Dekker: New York, 371–421.

TULADHAR S. & SMITH L.S. (2009): SONO filter: An excellent technology for save water in Nepal. SOPHEN 7, 18–24.

WANG Y. & SALVAGE K. (2005): Immobilization of uranium in the presence of $Fe^0_{(s)}$: Model development and simulation of contrasting experimental conditions. Appl. Geochem. 20, 1268–1283.

WARNER, S.D & SOREL, D. (2003): Ten years of permeable reactive barriers: Lessons learned and future expectations. In: Chlorinated Solvent and DNAPL Remediation: Innovative Strategies for Subsurface Cleanup, Henry, S.M., Warner, S.D., Eds, American Chemical Society: Washington, DC, ACS Symp., Ser. 837, 36–50.

WARREN K.D., ARNOLD R.G., BISHOP T.L., LINDHOLM L.C. & BETTERTON E.A. (1995): Kinetics and mechanism of reductive dehalogenation of carbon tetrachloride using zero-valence metals, J. Hazard. Mater. 41, 217–227.

WHO/UNICEF 2010. Progress on sanitation and drinking-water 2010 update, Geneva, Switzerland: WHO/UNICEF. http://www.unwater.org/downloads/JMP_report_2010.pdf (Access 2010/06/06).

WILSON E.R. (1923): The Mechanism of the corrosion of iron and steel in natural waters and the calculation of specific rates of corrosion. Indust. Eng. Chem. 15, 127–133.

YOU Y., HAN J., CHIU P.C. & JIN Y. (2005): Removal and inactivation of waterborne viruses using zerovalent iron. Environ. Sci. Technol. 39, 9263–9269.

ZHANG W.-X. (2003): Nanoscale iron particles for environmental remediation: An overview. J. Nanopart. Res. 5, 323–332.

ZHOU H. & SMITH D.W. (2002): Advanced technologies in water and wastewater treatment, J. Environ. Eng. Sci. 1, 247–264.

ZHU N., LUAN H., YUAN S., CHEN J., WU X. & WANG L. (2010): Effective dechlorination of HCB by nanoscale Cu/Fe particles. J. Hazard. Mater. 176, 1101–1105.