Remediation of Contaminated Groundwater Using a SpinChem Rotating Bed Reactor

*Competitive Sorption of Metal(loid)s in Complex Solutions under Varying Geochemical Conditions*

Pär Alapää

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Luleå University of Technology
Department of Civil, Environmental and Natural Resources Engineering
Abstract
The potential of utilizing a new form of chemical processing technology called SpinChem® Rotating Bed Reactor (RBR), in combination with different reactive materials, for the purpose of remediating multi-contaminated aquifers under changing environmental conditions, was investigated using laboratory studies and geochemical models. Four different reactive materials, or combinations thereof, were tested: heat-treated peat powder combined with zero-valent iron (ZVI); IronPeat, which consists of peat powder coated with a ferriferous hydrosol (FFH); and a powdered steel waste product. Results showed that the powdered steel waste was compatible with the technology while the peat-based sorbents were not. However, there were no indications that the kinetics of the sorption reactions increased. This was attributed to the fact that the rate-limiting steps, for the binding of the studied metal(loid)s onto iron oxide, are generally considered to be dependent on the later stages of the sorption process related to diffusion mechanisms and not to the rate of mass transfer through the bulk liquid phase, which is what primarily is increased through application of the SpinChem® RBR technology.

Keywords: Groundwater remediation, competitive sorption, SpinChem®

1. Introduction
Contaminated groundwater typically contains mixtures of multiple pollutants exhibiting different biogeochemical properties (USEPA 2017). Consequently, remediation measures intended to immobilize one contaminant may lead to increased mobility of another, this is generally known as pollution swapping (Stevens and Quinton 2009). The application of a single treatment technology may therefore not result in adequate amelioration of a multi-contaminated site (Bayer and Finkel 2005). Instead, the concept of multi-barrier systems has been introduced as a method for in-situ remediation of complex contaminant plumes. Multi-barrier systems utilise several reactive materials that are mixed or placed in a sequence within a permeable reactive barrier (PRB), removing contaminants either simultaneously or sequentially (Obiri-Nyarko et al. 2014). Another method frequently used for remediating contaminated groundwater is so-called pump-and-treat systems. With this approach, the groundwater is extracted from the subsurface by pumping so that it then can be remediated in above-ground treatment systems (USEPA 1996). This study aims to evaluate the potential of incorporating a new, innovative, form of chemical processing technology called SpinChem® RBR, in combination with different reactive materials, into pump-and-treat systems for the purpose of ameliorating multi-contaminated aquifers.

1.1 Aim and objectives
The objective of this thesis was to evaluate the potential of using the SpinChem® RBR technology, in combination with different reactive materials, for remediation of contaminated groundwater. Specifically, this study aims to elucidate whether the technology provides any advantage relative conventional pump-and-treat systems. The following research questions were formulated:

i) Does the SpinChem® RBR technology increase the reaction rate of the sorption process?

ii) What is the maximum sorption capacity of the different reactive materials for the studied contaminants?

iii) How are the technology and the different reactive materials affected by varied environmental conditions, specifically, varied pH and presence of dissolved organic matter?

1.2 Delimitations
The study has been limited to three different sorbents/comboination of sorbents; peat mixed with zero-valent iron (ZVI) in a 4:1 ratio, IronPeat and steel powder. A multi-contaminant solution including arsenic (As), copper (Cu), chromium (Cr) and zinc (Zn) was studied. These metals/metalloids were chosen since they are commonly found in high dissolved concentrations in contaminated soil and groundwater in association with various industrial areas. Specifically, sites contaminated with chromated copper arsenate (CCA), a chemical that in the past frequently has been used at wood impregnation plants,
tend to exhibit high concentrations of the aforementioned elements (Morell 2006). Also, high groundwater concentrations of these elements are associated with negative environmental impacts, e.g. disrupted ecosystems and decreased agricultural productivity (Tóth et al 2016).

2. Literature review
2.1 The SpinChem® RBR Technology
Heterogeneous reactions, which by definition involve the transfer of reagents from the bulk liquid phase to the hydrodynamic boundary layer surrounding the adsorbent material, are often limited by the rate of mass transfer. This is especially evident in traditional stirred tank reactor (STR) batch processes and often cannot be solved even by vigorous stirring or excessive amounts of solid phase. The SpinChem® rotating bed reactor (RBR) overcomes this by delivering very efficient convective mass transfer. As the reactor spins, a convective transport flow is induced resulting in increased mass transfer and faster reaction rates (fig 1.).

![Figure 1. Schematic illustration of the SpinChem® Rotating Bed Reactor (RBR). Arrows indicate liquid flow direction (SpinChem® 2017a).]

2.2 Sorption kinetics
The time it takes for sorption processes to reach equilibria is referred to as sorption kinetics. This is controlled by four sequential steps included in the progress of the sorption process (Worch 2012):
1. Transport of the adsorbate from the bulk liquid phase to the hydrodynamic boundary layer localized around the adsorbent particle.
2. Transport through the boundary layer to the external surface of the adsorbent, termed film diffusion or external diffusion.
3. Transport into the interior of the adsorbent particle (termed intraparticle diffusion or internal diffusion) by diffusion in the pore liquid (pore diffusion) and/or by diffusion in the adsorbed state along the internal surface (surface diffusion).
4. Energetic interaction between the adsorbate molecules and the final adsorption sites.

Typically, the first and fourth steps are relatively fast. Instead it is the two middle steps that usually are the rate-limiting ones. Of these, film diffusion rate is affected by stirring velocity, due to the reduction of boundary layer thickness, whereas intraparticle diffusion is not. It is also noteworthy that internal diffusion occurs by two simultaneous mechanisms, pore and surface diffusion. It is often difficult to differentiate the mass transfer effect of the respective steps. However, it is generally assumed that one mechanism is prevalent and thus, it is sufficient to only include that mechanism in subsequent kinetic modelling (Worch 2012).

2.3 Reactive materials
2.3.1 Zero-valent iron (ZVI)
Zero-valent iron (ZVI or Fe⁰) is the most widely utilized reactive material for PRBs. As of 2004, approximately 60% of the PRBs installed were iron-based (Henderson and Demond 2007). ZVI has been frequently applied in the remediation of a wide range of contaminants, such as heavy metals (Morachi and Calabró 2010; Ponder et al 2001), chlorinated organics (Arnold and Roberts 2000; Choi and Lee 2012; Kustov et al. 2011), nitroaromatics (Mu et al. 2004; Yin et al. 2012) and metalloids (Neuman et al 2013; Olegario et al. 2010). There are also other benefits associated with using ZVI, including that it is an abundant and relatively cheap material that is also non-toxic. Since the technology was introduced at the beginning of the 1990s, over 200 ZVI PRBs have been installed (Fu et al. 2014).

2.3.1.1 Contaminant removal mechanisms
The reduction potential of ZVI is high, ~440 mV, making it a very effective reductant for
oxidized contaminants. In the presence of dissolved oxygen (DO), ZVI also has the potential to treat various reduced contaminants (Fu et al. 2014). However, the introduction of DO into a ZVI system might catalyse reactions that have the potential to undermine the overall function of the system. Currently there does not exist a general way of predicting the net effects that the competing enhancing, and/or deteriorating processes associated with increased oxygen concentration will have on ZVI performance. ZVI also has the potential to remove contaminants through several other reaction mechanisms, such as adsorption, co-precipitation and surface complexation. Other factors that influence the effectiveness of these mechanisms include, pH and amount of dissolved ions (e.g. $\text{HCO}_3^-$, $\text{SO}_4^{2-}$ and $\text{Ca}^{2+}$) present in solution. Whether or not the effects of these are positive or negative is a complicated issue and depends on contaminant type as well as environmental factors. In many cases the impacts of different operating conditions are not properly understood (Sun, Huang and Guan 2016). A study by Henderson and Demond (2007) suggests that factors that control iron reactivity, including pH, eH, nitrate-, and bicarbonate concentrations, seems to exert more influence on the long-term performance of ZVI systems than other variables that have previously received a lot of attention in the literature, e.g. DO, total dissolved solids (TDS) and SI of carbonate minerals.

### 2.3.1.2 Limitations and methods for enhancement

Two of the major limitations of the ZVI technology are, narrow pH-range in which the reaction remains efficient, and loss of reactivity with time. The latter is caused by precipitation of secondary hydroxide- and carbonate minerals. To counteract these issues, as well as other problems associated with the ZVI-technology, several measures can be taken. These include different modifications of ZVI particles, e.g. decreased particle size or physical- and chemical enhancement. It is also possible to combine ZVI with other materials for improved efficiency (Guan et al. 2015). Fu et al. (2014) notes that the bulk of ZVI related research has been focused on parameter optimization, but that the main limitation with the technology is actually related to decreased performance over time. Therefore, the authors argue, more research efforts should instead be directed towards increasing the longevity of ZVI-systems, for instance by combining ZVI with other low-cost materials. Furthermore, the authors suggest that laboratory studies should use contaminant mixtures that as closely as possible resembles field conditions. Despite the various drawbacks of the technology and limited understanding of the reactive processes involved, there are very few reported cases where ZVI-based PRBs have actually failed (Henderson and Demond 2007). Even for ZVI PRBs with operating times above 15 years, the need for maintenance is typically relatively low (ITRC 2011).

#### 2.3.2 Nanoscale Zero-Valent Iron (nZVI)

Nano-sized particles containing zero-valent iron (nZVI) can be injected directly into the ground, forming a so-called reactive treatment zone. The smaller particle size results in higher reactivity, primarily due to larger surface area (Tratnyek 2006). As a result, nZVI has the ability to treat contaminants that micro-sized counterparts have not been able to. Another advantage using nano-sized particles is that the degradation of contaminants is typically more complete, thus decreasing the amount of undesirable by-products. Injection of nZVI is generally considered to be a more potent technique than traditional PRB-designs (Guan et al. 2015).

The larger surface area to mass ratio associated with nanomaterials has the potential to reduce both mass of material as well as energy used in the manufacturing process, resulting in lowered costs. The low toxicity, relatively high mobility within porous media, high reactivity and low cost of nZVI has made it the most extensively studied nanomaterial for water remediation purposes (Crane and Scott 2012). There is a growing interest in nZVI. In the last decade about 16% of the articles published on ZVI, dealt with nano-scale particles (Fu et al. 2014). In the United States, nZVI is already an established method for in-situ remediation, but in Europe the technology has not yet gained widespread acceptance (Mueller et al. 2012).

#### 2.3.2.1 Limitations

Two of the main processes responsible for reducing the effectiveness of nZVI are agglomeration and passivation. The former refers to the mechanism where nano-particles...
are attracted to each other aggregating into larger, micro-sized particles, lowering their mobility and effective surface area. Passivation results from nZVI reacting with groundwater constituents, e.g. nitrate and dissolved organic carbon, instead of the contaminants (Guan et al. 2015).

Another issue hindering the usage of nZVI for full-scale field application is cost. Compared to conventional micro-sized zero-valent iron (mZVI), nano-sized particles are significantly more expensive per unit of weight, typically in the order of 10-100 times more. This price difference is related to the manufacturing processes. Currently, there are several physical and chemical nZVI-synthesizing methods available including e.g. chemical vapour deposition, inert gas condensation, pulsed laser ablation, spark discharge generation, sputtering gas-aggregation, thermal decomposition, thermal reduction of oxide compounds, hydrogenation of metallic complexes and the aqueous reduction of iron salts. The price as well as the quality of the material produced by the respective methods differ. In general, material synthesized by cheaper methods tend to be more prone to agglomeration (Crane and Scott 2012).

A recurring problem with previous lab studies that only analysed simple solutions is that they tend to over-estimate the contaminant removal capacity of nZVI, relative to what has subsequently been revealed to be the actual field performance in treating complex contaminant mixtures. This predicament was clearly illustrated in a study by (Crane et al. 2011), in which nZVI was applied with the intention of treating uranium-contaminated groundwater. The lab study indicated that the method was highly effective. But when tested in field conditions, while first rendering comparable results to the lab analyses, remobilization of the uranium was observed over extended time periods. This was attributed the presence of complexing agents, predominantly carbonate, forming insoluble complexes with the partially unreduced uranium ions. The effect of complexing agents is a factor that for the most part has been neglected in the literature thus far. The intuitive strategies for dealing with this issue would either be to add an excessive amount of nZVI from the start, or continuously add more. However, the consequences of these approaches, as well as the influence of complexing agents in general, has probably not been sufficiently understood from a geochemical perspective and there is a need for more research efforts devoted to these topics (Crane and Scott 2012).

2.3.2.2 Ecotoxicology
Another pressing issue that warrants further attention is that of the potential ecotoxicological effects of nZVI remediation. There are still questions regarding the faith and effect in/on the environment. There seems to be an underlying consensus in the literature that oxidized nZVI-particles do not possess a threat from a toxicological standpoint. Although, the effect that unpacified nZVI might have on living organisms that come in direct contact with the material is still not clear (Guan et al. 2015). Also, extraction of the nanomaterial and the associated contaminants is generally not feasible and there therefore exists an underlying risk for remobilization, should the surrounding environmental conditions change (Crane and Scott 2012). But in general, since the mobility of nZVI is so low due to its high reactivity, the likelihood of any adverse environmental effects is quite low. A more interesting issue is what secondary products may be formed after nZVI treatment and how the faith of those products can be monitored satisfactorily. Also, long-term performance after surface modification is largely unknown (Tratnyek, and Johnson 2006). Although the number of studies on how nZVI behaves in the environment is relatively low, since the technology itself is rather new, it is reasonable to assume that the behaviour of nZVI is similar to that of conventional micro-sized ZVI, which is an extensively studied topic. The most prominent health risk associated with nZVI is actually inhalation when handling the material. But as long as the necessary precautions are taken, that risk is more or less eliminated (Crane and Scott 2012).

2.3.2.3 Methods for enhancement
There have been several approaches developed for improving the nZVI technology and for dealing with the issues discussed in the previous section. One such method is to support nZVI onto other material, e.g. activated carbon or zeolite (Fu et al. 2014). When choosing the right type of modification,
it is important to consider the site-specific conditions. One approach that has proven rather successful is to create nZVI-alloys with nobler metals, Pd being the most promising thus far. Bimetallic alloys have received a lot of attention in the United States but have not yet been applied at field scale in Europe. Bimetallic nZVI typically results in high reactivity but short longevity. So, they are best suited for sites where the migration time to the contaminant plume is short. Cost and ecotoxicology are also important aspects to consider since noble metals might be toxic and more expensive. Reactivity differs between different alloys, in some cases it is several orders of magnitude better than lone nZVI, in some not. Thermal treatment can also be used to improve nZVI properties (Crane and Scott 2012).

2.3.2.4 The future of nZVI remediation
Nanotechnology is one of the most rapidly growing sectors of the economy and soil/groundwater remediation using nZVI is a promising technique that has seen a lot of advancements in recent years. However, a crucial aspect required in making way for the future development of the technology is that a common testing framework is established so that results from different studies more easily can be compared. More focus need also be directed at cost reduction (Crane and Scott 2012). Furthermore, there are relatively few studies available on the toxicological impact of nZVI on aquatic and soil organisms, and the literature examining the potential phytotoxicity of nZVI show inconclusive findings. (Stefaniuk et al. 2016). Modified versions of nZVI have the potential to increase the remedial effects, but at the same time, their subsequent fate in the environment is still poorly understood (Tratnyek 2006).

2.3.3 Iron oxides
There exist several naturally occurring iron oxides, -hydroxides and -oxyhydroxides. Examples include, goethite, ferrihydrite and hematite. For simplicity, the term iron oxides will from now on be used when referring to this group of minerals. Many iron oxides have high adsorption capacities for both As(III) and As(V) as well as various oxyanions, e.g. SO$_4^{2-}$ and PO$_4^{3-}$ (Carabante 2009). Gupta et al. (2011) showed that the magnetic properties of iron oxides could be beneficially combined with carbon nanotubes for the removal of chromium ions. Studies have also shown that hexavalent chromium can be effectively adsorbed onto iron oxide coated sand material (Satpathy and Chaudhuri 1995; Bailey et al. 1992). As previously discussed, specific surface area is a key factor controlling the adsorption capacity of a material. For this reason, iron oxide nanomaterials (INMs) have gained an increasing amount of interest in recent years. Different forms of INMs have been successfully applied in the remediation of heavy metals and organic contaminants. However, there are still relatively few studies evaluating the different aspects of this technology. The potential limitations to the technology are similar to those described in the previous section on nZVIs, e.g. aggregation, competitive adsorption and ecotoxicological effects (Xu et al. 2012). Also, separating the INMs from the treated solution tends to be a problematic issue (Mohan and Pittman 2007).

2.3.4 Peat
Peat is a relatively complex soil material consisting of a conglomerate of porous organic matter at different stages of decomposition. The material has a large surface area and possesses high adsorption affinities for a variety of metals due to high cation exchange capacity related to the large number of polar functional groups contained in its major constituents, lignin and cellulose. Peat is such a good adsorbent of heavy metals, that naturally occurring peat bogs often are utilized for mineral exploration purposes. It is also abundantly occurring, making it comparatively inexpensive (Bailey et al. 1999).

2.3.4.1 Areas of application
Mondal et al. (2016) investigated the possibility of applying peat as a reactive medium in PRBs, mediating the biodegradation of trichloroethene (TCE). The results of the study indicated that peat was very effective in supporting the anaerobic conditions required for reductive dechlorination of TCE to ethene. A column study conducted by Rasmussen et al. (2002) showed that a mixture of sand and peat as a PRB-material can be used to remediate creosote-contaminated groundwater. However, some modifications might be necessary in order to achieve a fully satisfactory treatment. Koivula et al. (2009) used batch- and column-
tests to evaluate the applicability of peat as an adsorbent in landfill material. The results indicated that peat has the potential to act as an efficient adsorbent for the removal of heavy metals and arsenic in landfills. Peat has also frequently been utilised in filter beds for the treatment of contaminated waters. Peat is usually, in the conditions it typically occurs, a very slowly decomposing material. But when used in filters, the decomposition rate might increase leading to deteriorating performance with time (Kalmykova et al. 2009).

2.3.4.2 Adsorption mechanisms in relation to changing environmental conditions
There exist a wide variety of different peat types, differing in chemical and physical attributes. Which adsorption mechanism that dominates depends on type of peat as well as various other factors including, for instance, pH and ionic strength (Bailey et al. 1999). The main metal adsorption mechanisms are believed to be ion exchange, surface adsorption and complexation. It should, however, be said that this is a contentious topic still under debate (Brown et al. 2000).

Gupta et al. (2009) showed that the removal of Cu and Ni by peat was most effective in the pH-range 4.0-4.5 (in a studied pH-range of 2.0-6.0). In general, the optimal pH-range for metal removal using peat is typically somewhere around 3.5-6.5 (Brown et al. 2000). Kalmykova et al. (2009) studied peat filter adsorption rates for a complex solution containing As, Cd, Cu, Cr, Ni, Pb and Zn under changing physical factors, e.g. varying pH, metal concentration, and addition of DOC and NaCl to the system. The adsorption capacity for Cd, Cu, Zn, Ni and Pb remained high irrespective of environmental conditions. Although, the removal efficiency was briefly reduced when adding NaCl. As and Cr was, on the other hand, not removed as efficiently as the other metals. Likely, the reason for this is that As and Cr occurs as anions in the neutral to basic condition (pH 6.7-8.0) at which the study was conducted. When studying a multi-component system containing Cu, Ni and Pb, Liu et al. (2008) found that the adsorption rate of all metals increased as pH went up.

2.3.4.3 Treatment of complex solutions
A study by Qin et al. (2006) indicated that the adsorption of heavy metals onto peat in a multi-contaminant system decreased relative to single component systems. Furthermore, the XAS (X-ray adsorption spectroscopy) analyses showed that Pb and Cu predominantly bounded to carboxylic groups in the peat. Despite the fact that the adsorption capacity of the individual metals present in multi-contaminant systems typically decreases, the total adsorption capacity might actually increase (Brown et al. 2000) Ringqvist, Holmgren and Öborn (2001) investigated how metal adsorption onto peat from wastewater was affected by varying composition of the treated complex solutions. They found that the removal efficiency was greatly dependent on the composition. In a sulphidic mine leachate solution, in which the metals mainly occur as dissolved ions, the removal efficiency was high compared to that of the landfill leachate, in which the metals primarily were bound to carbonate- and organic complexes. Other factors that might influence peat adsorption capacity include, for instance, diffusion and temperature (León-Torres et al. 2012).

2.3.4.4 Limitations and methods for enhancement
Although peat can act as an efficient adsorbent of contaminants, there are some drawbacks associated with applying natural, unmodified, peat for remediation purposes. These disadvantages include, low mechanical and chemical stability, high water affinity as well as a propensity to shrink or swell and leach fulvic acids (Crini 2006). It is, however, possible to improve the effectiveness of the peat material by pre-treatment with relatively cheap reagents (Bailey 1998). For example, NaOH, HCL or citric acid can improve the sorption capacity and settling ability of peat (Leiviskä et al. 2018). It is also possible to recover the previously adsorbed metals and regenerate the peat through acid elution, while still maintaining the original sorption ability of the material (Brown et al. 2000). However, recovery is not always economically feasible for metals that are strongly bound to the peat, e.g. Cr(VI) where almost no desorption occurs in low caustic conditions and in high caustic conditions the peat itself becomes unstable (Sharma and Forester 1993). Peat have also been successfully combined with other adsorbents such as activated carbon, zeolites and resins for desalination and chromium removal (Aghakhani et al. 2011).
3. Methods

3.1 Material characterization
Total solids (TS) and loss on ignition (LOI) of the sorbents were determined according to Swedish Standard SS 02 81 13 (table 8 appendix). A sieve analysis (gradation test) was performed on the steel powder in order to estimate the particle size distribution of the material.

3.2 Solutions
The solutions were prepared by diluting the source chemicals, As₂O₃, K₂Cr₂O₇, CuCl₂ x 2H₂O and ZnCl₂, in deionized water. In order to determine the influence of organic matter on the system, humic acid was added corresponding to a concentration of 100 mg/l. Potassium nitrate, 0.1 M KNO₃, was used as an electrolyte background solution to prevent chemical reactions between the metals in the solute.

3.3 Sorbents
Four different materials were used as sorbents in this study; zero-valent iron (ZVI), peat powder, Iron-peat and steel powder. Heat-treated peat powder (peat) was obtained from Geogen Produktion AB. This company produces heat-treated peat granulate as an environmentally compatible oil-adsorption agent. During its production, particles smaller than 0.5 mm are discarded and considered as residues. Iron-peat consists of peat powder mixed with Ferriferous hydrosol (FFH) and water (1:1:0.5). The hydrosol is a colloidal suspension of Fe(II) and Fe(III) hydrated compounds, acting as a binder for wastewater pollutants. FFH is produced from Fe waste during the process of electrolysis. Zero-valent iron was obtained from SSAB Merox AB, Sweden. The material contains 91% iron and 98% of particles are smaller than 1 mm. Steel powder was obtained from Scania Ferruform AB. The material is a waste product generated in their manufacturing process and it contains about 15% iron with a particle size ranging from 65-315 µm.

3.4 Adsorption tests
To estimate the maximum adsorption capacity of the sorbents, a one-step batch leaching test was performed according to European Standard SS-EN12457-2. For the first series of batch tests using the SpinChem® RBR S3 rotating bed reactor (fig. 2), the centrifuge was attached to a stand and lowered into the vessels containing 100 l of solution. The centrifuge was operated at a constant rotating speed of 600 rpm. A glass rod was placed in the vessel to act as a vortex disruptor. For the second series of tests, The SpinChem® reactor was operated inside a SpinChem® flower-baffled jacketed reaction vessel (fig. 1) containing 1000 ml of solution. The device was then operated at a constant rotating speed of 400 rpm. The influence of pH was investigated by performing pH-stat tests using an automatic titrator (Titra Lab 90, software TimTalk 9 version 2.1). 0.1 M HNO₃ was used as a titrant.

3.5 Sampling and analyses
100 ml and 4.9 ml of solution were pipetted for DOC and metal analyses, respectively. This was done at the start and after 10 min, 30 min, 1 h, 2 h, 5 h and 24 h for the 100 l batches; and after 1 h, 5 h and 24 h for the 1000 ml batches. 2% Nitric acid, HNO₃, was added to the samples to prevent precipitation of metals before analyses. pH and electrical conductivity (EC) were also measured for all samples. The leaching tests were filtered through 0.45 µm cellulose filters. The extracted solutions were subsequently analyzed with ICP-OES.

3.6 Geochemical modelling
Multi-surface geochemical models simulating adsorption of arsenic, chromium, copper and zinc were designed using the software Visual Minteq version 3.1 (Gustafsson 2018). The model included speciation in the dissolved phase, sorption/desorption of anions and cations to ferricydrate and solid organic matter (SOM). Sorption to Iron oxides was simulated using the generalized two-layer model.
(GTLM) (Dzombak and Morel 1990). Complexation to organic matter was modelled using the Stockholm Humic Model (SHM). Equilibrium conditions were assumed. Furthermore, it was also assumed that the distribution of humic acids (HA) and fulvic acids (FA) in the SOM were 3:1.

4. Results

4.1 Sorption capacity

The batch leaching tests show that steel powder is the most efficient sorbent for all elements except with respect to chromium, which is most readily sorbed onto the mixture of peat and ZVI (fig. 3-7). The maximum sorption capacities of the respective sorbents are shown in table 1. These results are based on the L/S 1000 batch leaching tests, except for the sorption capacity of chromium for steel powder which was calculated based on the L/S 10 tests, as so little chromium were removed for the higher ratios (fig 5). Copper and zinc were completely removed from solution by the steel powder (fig. 6-7). Thus, the maximum sorption capacities for these elements are higher than what could be the determined from these tests. It is also relevant to note that pH increases to over 11 in the steel powder solutions, likely caused by leaching of calcium (fig. 8).

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<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Zn</th>
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<tr>
<td>Steel Powder</td>
<td>11.31</td>
<td>0.06*</td>
<td>&gt;11.66</td>
<td>&gt;12.02</td>
</tr>
<tr>
<td>Peat + ZVI</td>
<td>10.88</td>
<td>5.51</td>
<td>6.84</td>
<td>0.92</td>
</tr>
<tr>
<td>IronPeat</td>
<td>2.64</td>
<td>0.81</td>
<td>5.06</td>
<td>0.80</td>
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</table>

Table 1. Maximum sorption capacities (mg/g). Calculated from L/S 1000 batch leaching tests results.

*based on L/S 10 leaching tests
In general, the lowering of contaminant concentrations for all 100 l SpinChem® RBR batch tests were low (fig. 9-11). However, the volume of treated solution was large compared to the amount of sorbent used, i.e the L/S ratio was high (10 000:1 and 5000:1 for the first and second round, respectively). It can therefore be interesting to consider the contaminant removal, in mg metal(loid) per gram of sorbent, and compare that to the previously determined maximum sorption capacities (table 2). When doing so, the results for the peat-based sorbents are rather ambiguous.

For the combination ZVI and peat, the removal of anions in the first round of batch tests (10 g sorbent, i.e L/S 10 000) were similar to what could be expected based on the maximum sorption capacities. Making the same comparison for copper on the other hand, only about one-third was removed relative to what could be expected. Whereas the removal of zinc was higher than the maximum capacity. In the second round of tests (L/S 5000), the results are almost reversed. The removal of anions is significantly lower than expected whereas the removal of cations is similar to the maximum sorption capacity for copper and significantly higher for zinc (table 2).

For Iron peat, the removal of anions is low for L/S 10 000 and high for L/S 5000 compared to the maximum sorption capacities. Whereas the opposite true for copper, i.e high removal in the first test round with larger L/S ratios and lower in the second round. Zinc is removed to a large extent, compared to the maximum capacity, in the second round as well but still significantly lower than in the first round (table 3).

The contaminant removal observed for the steel powder is in general quite similar to what could be expected based on the maximum sorption capacities. Although, zinc removal is a bit lower than expected and copper removal is seemingly higher. But it is hard to say anything definitely for the latter since, as previously discussed, the maximum sorption capacity for steel powder with respect to copper is higher than could be determined by the leaching tests (table 4).

In summary, the results from the 100 l SpinChem® RBR batch tests are, as mentioned, ambiguous. However, the calculations above on contaminant removal are based on the observed concentration decreases, which are overall quite small. Taken into account sampling and analytical uncertainties, it is really hard to draw any definitive conclusions based on these results.
Figure 9. SpinChem® RBR packed with Peat/ZVI in 100 l batch tests using 10 and 20 g of sorbent material (L/S 10 000 and 5000, respectively).

Table 2. Metal(loid) sorption (mg/g) in SpinChem® RBR Peat/ZVI 100 l batch tests (concentration decrease x volume treated / weight of sorbent) compared to sorption capacities calculated from leaching tests (table 1).

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<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Zn</th>
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<tr>
<td>SpinChem® RBR Peat/ZVI L/S 10 000</td>
<td>10.30</td>
<td>5.34</td>
<td>2.80</td>
<td>1.60</td>
</tr>
<tr>
<td>SpinChem® RBR Peat/ZVI L/S 5000</td>
<td>1.53</td>
<td>-4.63</td>
<td>6.71</td>
<td>5.42</td>
</tr>
<tr>
<td>Max cap.</td>
<td>10.88</td>
<td>5.51</td>
<td>6.84</td>
<td>0.92</td>
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Figure 10. SpinChem® RBR packed with IronPeat in 100 l batch tests using 10 and 20 g of sorbent material (L/S 10 000 and 5000, respectively).

Table 3. Metal(loid) sorption (mg/g) in SpinChem® RBR IronPeat 100 l batch tests (concentration decrease x volume treated / weight of sorbent) compared to sorption capacities calculated from leaching tests (table 1).

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<tr>
<td>Max cap.</td>
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<td>0.81</td>
<td>5.06</td>
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Table 4. Metal(loid) sorption (mg/g) in SpinChem® RBR Steel powder 100 l batch tests (concentration decrease x volume treated / weight of sorbent) compared to sorption capacities calculated from leaching tests (table 1).

<table>
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<th></th>
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<th>Zn</th>
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<td>&gt;12.02</td>
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</table>

4.2.2 1000 ml

For IronPeat, the metal(loid) concentrations essentially remained unchanged for the 1000 ml SpinChem® RBR batch tests (fig. 12). The removal of contaminants was significantly lower than the maximum sorption capacities (table 5).

The combination of Peat and ZVI almost completely removed arsenic from solution after 24 h. Also, the concentrations of the other elements decreased somewhat (fig. 13), although the total removal was significantly less than the maximum sorption capacity (table 6).

After one hour the steel powder had removed all cations and 90% of the arsenic from solution. In the end, 95% of the latter was sorbed, which was essentially the same sorption capacity as observed in the leaching tests. Chromium showed almost no decrease in concentration but this was expected as this also was in line with the results from the leaching tests (fig. 14 and table 7).

Figure 12. Metal(loid) concentrations for IronPeat 1000 ml SpinChem® RBR batch test (L/S 100).

Table 5. Metal(loid) sorption (%) in SpinChem® RBR IronPeat 1000 ml batch tests (SC) compared to the corresponding sorption capacities calculated from L/S 100 leaching tests (LT) (fig. 4-7).

<table>
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<th>Cu</th>
<th>Zn</th>
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<td>7.49</td>
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<td>43.32</td>
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subsequent pH-stat tests instead focused exclusively on the steel powder.

The removal of arsenic decreased somewhat with increasing pH. Although, even at pH 11 the removal was almost complete. In order to determine the effect of organic matter on the system, humic acid was added. There were no indications that this had any significant effect on arsenic removal (fig. 15).

As previously discussed, there were essentially no removal of chromium at pH 11. But as pH decreases, chromium is adsorbed to a higher extent. At the lowest pH, all chromium is removed from solution. Again, organic matter does not seem to have much impact on the removal rate (fig. 16).

Essentially all copper is sorbed for all the tested conditions. Although, the reaction rate is slowed down as pH decreases, which is particularly clear at pH 3. Addition of humic acid also seem to slow down the kinetics somewhat (fig. 17).

For zinc the trend is similar to that of copper, with a slight decrease in sorption as pH goes down and a large decrease at pH 3. In fact, the concentration of dissolved zinc is more than doubled after the first hour at pH 3. In the presence of DOC the sorption rate significantly decreases. At pH 3, as well as when humic acid was added, the zinc concentration is lower after 5h than after 24h (fig 18).

![Figure 13. Metal(loid) concentrations for Peat/ZVI 1000 ml SpinChem® RBR batch test (L/S 100).](image1)

![Figure 14. Metal(loid) concentrations for Steel powder 1000 ml SpinChem® RBR batch test (L/S 100).](image2)

![Figure 15. Arsenic removal as an effect of pH and DOC.](image3)

4.3 pH-Stat tests

Since the results of the SpinChem® RBR batch tests indicated that the peat-based sorbents were not compatible with the technology due to clogging of the outer reactor filters, the
4.4 Geochemical modelling

For both of the studied anions, arsenate and chromate, the observed removal corresponds well to what the models predict. Although, for chromium the expected decrease with increased pH seem to start at somewhat lower pH values than the models anticipate (fig. 19-20).

The cations, copper and zinc, are both sorbed to a higher extent than the models predict, the only exception being the pH 7 experiment for zinc (fig. 21-22a). However, as previously discussed and as seen in figure 18, zinc was removed completely from solution after 5 h but then increases again at the last sampling occasion. Figure 22b shows model predictions regarding how copper is distributed between the dissolved phase, the iron oxide and the humic acids (DOM), over the studied pH-range. Copper is the only element that the models predict will be affected by addition of humic acid. Hence, partitioning is not presented for the other elements. The model indicates that copper should form complexes with the organic matter and to a lesser extent bind to the iron oxide. (fig. 22b). However, the experimental data show no decrease in sorption capacity with respect to copper as humic acid was added (fig. 22a).
Figure 19. Model prediction on arsenate sorption onto ferrihydrite as a function of pH (solid line) compared to recorded values from SpinChem® RBR 1000 ml pH-stat batch tests (squares).

Figure 20. Model prediction on chromate sorption onto ferrihydrite as a function of pH (solid line) compared to recorded values from SpinChem® RBR 1000 ml pH-stat batch tests (circles).
Figure 21. Model prediction on Zn(II) sorption onto ferrihydrite as a function of pH (solid line) compared to recorded values from SpinChem® RBR 1000 ml pH-stat batch tests (circles).

Figure 22a. Model prediction on Cu(II) sorption onto ferrihydrite as a function of pH (solid line) and addition of humic acid (HA, dashed line) compared to recorded values from SpinChem® RBR 1000 ml pH-stat batch tests (tilted squares).
5. Discussion

5.1 Kinetics
When studying the sorption kinetics of arsenate and chromate onto goethite, Grossl et al. (1997) concluded that sorption occurred in two consecutive steps. In the first, monodentate inner-sphere complexes were formed and in the second bidentate dittos. The first step was significantly faster than the second one. The study also showed that arsenate is more likely to form inner-sphere complexes with goethite, than is chromate. Thus, arsenate is more readily adsorbed in natural systems. Furthermore, varying electrolyte background concentration (NaNO₃) did not have an effect on arsenate or chromate sorption. Similar conclusions regarding the kinetics of arsenic sorption onto ferrihydrite were made by Fuller et al. (1993) and Luengo et al. (2007). Both studies observed an initial fast sorption occurring within the first five minutes followed by significantly slower reaction rates lasting for hours and even days. In both articles, the slower step was attributed to diffusion-driven processes. The latter study mentioned also showed that stirrer velocity did not affect the rate of arsenic sorption. Xue et al. (2009) conducted batch equilibrium experiments for multi-element solutions, including copper(II) and zinc(II), studying the sorption onto blast furnace powder. Equilibrium was reached already after 30 minutes (at pH 6), with no more sorption occurring for the remainder of the experiment. The authors attributed the adsorption that took place at low pH-values to ion exchange reactions whereas sorption at higher pHs were believed to occur through the formation of monodentate inner-sphere complexes.

As seen in figure 15-16, the concentrations of both arsenate and chromate decrease most rapidly in the first, 1 h, sampling interval, followed by slower sorption rates at the subsequent samplings. This could be interpreted as being in agreement with the conclusions regarding arsenate and chromate sorption in the studies cited above. Also, as could be expected based on the findings from Grossl et al. (1997), arsenate has a higher sorption affinity to ferrihydrite than chromate. However, the slower sorption rates may of
course also be caused by successively lower concentrations of the contaminants in solution. The potential advantage of using the SpinChem® RBR technology lies in an increased rate of mass transfer of reagents through the bulk liquid phase to the sorbent particle. But for contaminants such as arsenate and chromate, where the rate-limiting step of the sorption process is related to diffusion mechanisms, application of the SpinChem® RBR technology is not likely to increase the overall sorption rate. As previously mentioned, the sorption mechanisms for the studied cations are ion-exchange and monodentate complexation depending on the pH of the solution (Xue et al. 2009). Therefore, since these are relatively fast mechanisms compared to the bidentate complexation of arsenic and chromium, the likelihood that application of the SpinChem® RBR technology will lead to faster reaction rates is perhaps higher for the cations than for the anions studied. And, as seen in figure 17-18, copper and zinc are completely removed after the first hour. However, as noted by Plazinski et al. 2009, transport of the contaminants through the bulk liquid phase is typically not the limiting factor for sorption reactions even when conventional mixing devices are used. I.e. even though the sorption mechanisms for copper and zinc are relatively faster than those for arsenate chromium, they are still probably much slower than the time required for transport of solute through the bulk of the solution.

5.2 Sorption capacities
Of the three sorbents studied, steel powder had the highest sorption capacity for all metal(loid)s except for chromium, which was essentially not sorbed at all by the steel powder at unaltered pH (table 1). Adegoke et al. (2013) reviewed the literature on iron oxide sorption capacity for various oxyanions, including arsenate and chromate. For the former, the sorption capacities were found to be in the range 39.8 µmol/g-70.4 mg/g and for the latter in the range 3.13 µmol/g- 6.0 mg/g. Bekényiová et al. (2015) studied the sorption capacities of both natural and synthetic iron oxides (goethites and hematites) with respect to copper and zinc. A synthetic goethite was shown to have the highest sorption capacities, 2.8 mg/g and 1.8 mg/g for copper and zinc, respectively.

Relative to the studies cited above, the steel powder used in the present work has sorption capacities that lay somewhere in the mid-range for arsenate sorption and significantly higher with respect to copper and zinc. However, it is difficult to compare results regarding the sorption capacities of different materials due to differences in experimental setups etc. Instead, it is perhaps more relevant to discuss the potential of the sorbents used in this study relative to each other. As mentioned, steel powder has the highest overall sorption capacity. Another advantage of the steel powder is that it is a waste product that Scania Feruform AB, the steel manufacturer generating the product, has no use for. In fact, they are willing to reimburse actors willing to handle the disposal of the material.

Comparing the two peat-based materials, the combination peat and ZVI has the highest removal capacity for all metal(loid)s. This is no surprise since the ratio between peat powder and ZVI is the same as that between peat powder and ferriferous hydrosol (FFH), 4:1, but while ZVI is composed of almost pure iron, 91%, the FFH only contains about 12% iron. However, both the peat-based materials clogged the filters of the SpinChem® reactor and did not perform as well as could be expected (fig. 12-13; table 5-6). Therefore, some kind of modification of the materials is necessary to make them compatible with the SpinChem® RBR technology, e.g. addition of filter sand. But this will of course lead to increased costs. Instead, what the present work indicates is that the steel powder has the greatest potential to be used in combination with the SpinChem® RBR technology, both with respect to metal(loid) removal as well as from an economic perspective. The material also provides a pH buffering capacity due to calcium leaching (fig. 8), making it, potentially, particularly well-suited for treatment of low-pH groundwater.

5.3 Influence of changing environmental conditions
Arsenate is essentially completely removed across the whole pH-range with a slight decrease at the highest pH-value. This is also consistent with the corresponding model prediction (fig. 19). Chromate sorption is slightly lower than what the model predicts but
follows the expected trend with decreased sorption as pH increases (fig. 20). The cations are sorbed to a higher degree than predicted, with the exception of zinc at pH 7 (fig. 21-22). Although as mentioned, all of the zinc was sorbed at the 5 h sampling occasion but was then desorbed again at the last sampling. This trend with zinc remobilization is also observed at pH as 3 as well as when humic acid was added (fig. 18). The steel powder contains significant amounts of zinc (table 9 appendix), that is likely leached at the beginning of the tests, causing the increased concentrations seen after the 1 h sampling interval at pH 3 and when humic acid was added. Contrary to model predictions, humic acid does not influence copper sorption (figure 22a-b). A possible, albeit not very likely, explanation for this is that the organic complexes formed occur predominantly in the coarse colloidal phase, i.e. 0.45-12 µm (Vignati & Dominik 2003). Thus, it would be possible that these complexes are excluded from the analyzed dissolved phase when filtered.

6. Conclusions

- Steel powder showed the highest removal capacity for all studied metal(loid)s except chromium.
- The peat-based sorbents clog the filter of the SpinChem® reactor and are therefore, presently, not compatible with the technology. Modification of the material, e.g. by addition of filter sand, could perhaps solve this issue. Although, this might mean that destruction of the used sorbent, e.g. by combustion, will be less favourable.
- The steel powder is, on the other hand, compatible with the SpinChem® RBR technology, in the sense that it sorbs contaminants to the predicted extent, based on leaching tests. However, there is no indication from the present study that the SpinChem® RBR technology actually increases the reaction rates for the studied metal(loid)s. Nor is it likely, based on the literature study conducted, that this will be the case since the rate-limiting step for the studied contaminants is related to the later stages of the sorption process and not to the transfer of solute through the bulk liquid phase, which is what is accelerated when applying the SpinChem® technology.
- Disregarding the issue of sorption kinetics, the SpinChem® technology provides another potential benefit, relative to conventional pump-and-treat systems, in that the spent sorbent is easily separated from the solution after treatment.
- Since the steel powder is considered an industrial waste product, there are also economic incentives for utilizing the material.
- The high calcium content of the steel powder also provides the material with a buffering capacity, potentially making it particularly well-suited for treatment of low pH groundwater.

7. Suggestions for further studies

The results from this study indicate that, out of the studied materials, steel powder has the highest potential to be beneficially combined with the SpinChem® RBR technology, both with respect to metal removal capacity as well as from an economic perspective. Hence, further studies should focus on better understanding the sorption mechanisms of this material. Specifically, more detailed investigation of the steel powder sorption kinetics is needed to definitely elucidate whether it provides increased reaction rates or not. However, as discussed above, the SpinChem® RBR technology is not likely to increase the reaction rates for the studied metal(loid)s and thus, it would perhaps be more relevant for subsequent work to instead study sorption of other contaminants.

8. Acknowledgements

This master thesis constitutes the final part within the environmental geochemistry specialization at the graduate programme in exploration and environmental geosciences at Luleå University of Technology. The work corresponds to 30 ECTS credits and has been running from January to June 2018.
First and foremost, I would like to thank my thesis advisor Jurate Kumpiene for giving me the opportunity to conduct this degree project, as well as, through her knowledge and experience, providing useful comments, remarks and engagement throughout the writing of the thesis. I would also like to thank the rest of the personnel at the department for welcoming me into your group. In particular, I would like to express my sincere gratitude towards Alfreda Kasiuliene and Ivan Carabante. Alfreda, for assistance in various aspects, including laboratory work and geochemical modelling. Ivan whom, with his chemical expertise, gave insightful feedback that helped improve the quality of the thesis. He also kindly shared his office with me and provided interesting discussions on both work-related issues as well as a wide range of other engaging topics. I would also like to mention Desirée Nordmark who helped with the laboratory equipment from time to time. Furthermore, I would like to express my appreciation towards Erika Kämäräinen for reading and commenting on my paper. Last, but definitely not least, I would like to thank Eric Lundin at Geogen Produktion AB for funding this research study.

Almedalen, June 2018
Pär Alapää

10. References

Environmental Science & Technology, 34(9), 1794-1805.


environment research, 67(5), 788-790.


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Appendix
Part A – Material characterization

Table 8. TS and VS for the sorbents included in the study. Negative values (increased mass) is caused by oxidation of the material.

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Table 9. Element analysis of steel powder.

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<th>Co</th>
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</tr>
<tr>
<td>st.dev.</td>
<td>0.00</td>
<td>0.00</td>
<td>72.37</td>
<td>12.92</td>
</tr>
</tbody>
</table>
Part B – Geochemical modelling
L/S 100 models for peat-based sorbents

Figure 23a. Model prediction on metal(loid) sorption onto IronPeat at L/S 100 as a function of pH (solid line) compared to recorded values from batch leaching tests.

Figure 23b. Model prediction on zinc partitioning onto different phases.
Figure 24a. Model prediction on metal(loid) sorption onto Peat/ZVI at L/S 100 as a function of pH (solid line) compared to recorded values from batch leaching tests.

Figure 24b. Model prediction on zinc partitioning onto different phases.