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Removal of critical metals from waste water by zero-valent iron

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1. Introduction

Critical metals, defined as metals with growing economic importance that might be susceptible to future scarcity, are present in industrial waste waters. The European Union (European Union, 2010) and the Austrian Research Promotion Agency (FFG, 2012) designate the following metals as (potentially) critical: beryllium (Be), magnesium (Mg), manganese (Mn), nickel (Ni), cobalt (Co), zinc (Zn), chromium (Cr), aluminium (Al), gallium (Ga), indium (In), rare earth elements (REE), germanium (Ge), antimony (Sb), niobium (Nb), tantalum (Ta), tungsten (W), vanadium (V), molybdenum (Mo) and platinum group elements (PGE). However, they are mostly not recovered in standard chemical-physical waste water treatment as they often have no negative impact on the environment. In this study, a new approach to remove these metals from synthetic aqueous solutions and real industrial waste water samples using zero-valent iron (ZVI) in an fluidized bed reactor (FBR) (Ferrodecont process) as a first step for subsequent recovery is presented.

The Ferrodecont process was developed between 2006 and 2012 parallel to a similar development in Romania (Gheju and Balcu, 2011) for the remediation of contaminated sites (Müller et al., 2014). It is based on the corrosion of ZVI by water which is accelerated by reducible dissolved species (Gheju, 2018) and a

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reaction between their corrosion products and dissolved metal species which are removed from the solution due to reduction and/or adsorption and/or precipitation processes. The complex nature of the underlying chemical reactions has been discussed intensely (Makota et al., 2017). Another example for the use of zero-valent metals is the cementation of silver onto zinc particles in the Merril-Crowe process (Gamboa et al., 2005).

In this study, the feasibility of the process for the fixation of other elements, i.e., critical and potentially critical metals, is demonstrated. In contrast to traditional industrial waste water treatment technologies the focus is on recycling rather than on disposal. The results of this project form the basis to enable a recycling process for dissolved (potentially) critical metals from waste waters.

The recycling of critical metals contributes significantly to cleaner production as mining of many of these metals is associated with severe environmental pollution, e.g. the release of radioactivity by processing of REE ores (Wall et al., 2017). However, the recycling rates of critical metals are generally low, i.e. < 1% for REE, Ga, Ge, In and <25% for W (United Nations Environment Programme, 2011). Recently, recycling processes for several critical metals from solid wastes have been developed, e.g., for Dy and Nd from permanent magnets (Yoon et al., 2016), for the Ga from GaN-containing e-waste (Swain et al., 2015) or for In from liquid crystal displays (Zhang et al., 2015). In order to recycle critical metals from industrial waste waters they have to be removed from the aqueous solution in a first step. However, for industrial waste waters removal processes are mostly not applied due to low concentrations, e.g. one to hundreds of mg/L for rare earth elements (Li et al., 2013), and lacking restrictions for the discharge of non-environmentally harmful metals, e.g. for REE in the Austrian Waste Water Emission Ordinance (Austrian Federal Minister for Agriculture and Forestry, 1996), although many recycling processes for solid wastes involve hydrometallurgical steps (Tuncuk et al., 2012) which might be applied for waste water, too. Consequently, the current study aims for a removal of critical metals from industrial waste waters by ZVI.

Iron and iron compounds, also in the form of nanoparticles (Tosco et al., 2014) or iron-containing solid wastes (Iakovleva et al., 2016), are frequently used in the field of contaminated site remediation, according to different narratives either by using ZVI as reducing agent or by presenting it as a generator of adsorbing (hydroxides, oxides) and reducing (Fe^{II}, H/H_2) agents (Noubactep, 2015). Adsorbing agents, created in-situ from ZVI, are iron hydroxides, which have also been shown to be the controlling factor in the mobility of heavy metals in the environment (Cornell and Schwertmann, 2003). The use of metallic iron for water treatment was patented already in 1857 by Dr. Medloch in the UK, applied for the water supply of Antwerp, Belgium, in 1879 and established in Europe already around 1890 (Devonshire, 1890) and interactions in aqueous solution have also been investigated in that time (Fenton, 1894). Since then, a broad range of applications has evolved (Mwakabona et al., 2017) including ZVI-based permeable reactive barriers for groundwater remediation (Henderson and Demond, 2007) and controversial discussions about the chemical principles behind the observed effects (Noubactep, 2015). Generally, ZVI is regarded as (1) a reductant for some species, (2) an adsorbent for other species, (3) a coagulant for various anionic species and (4) a long-term supplier of Fe^{2+} for activation of oxidation processes (Makota et al., 2017). In water, ZVI dissolves oxidatively and forms Fe^{II} species which former transform into Fe^{III} species and mixed Fe^{II} and Fe^{III} species including solid (hydr)oxide phases (Noubactep, 2010). Several studies show that iron and iron hydroxides can fix Be (Novikov et al., 1977), In (Koleini et al., 2010), Nd (Armstrong and Wood, 2012), Ge (Pokrovsky et al., 2006), Sb (Enders, 1996), Nb (Olveira et al., 2008), Mo and W (Gustafsson, 2003), Mn and V (Morrison et al., 2002), Ni (Calabrò et al., 2012), Co (Üzüm et al., 2008), Zn (Kishimoto et al., 2011), Ga (Xu et al., 2007) and Al (Manceau and Gates, 2013), whereas no studies on Ta removal by iron phases were found. However, although several improvements like sulfidation (Wang et al., 2018) were tested, none of these studies included the use of an FBR. One group of studies used iron compounds for the fixation of Sb (Wu et al., 2010), Co (Dyer et al., 2012), rhodium (Rh) (Krehula and Music, 2010) and Zn (Perales-Perez and Umetsu, 2002) which leads to a salination of the treated waters and thus has a negative effect on the recycling of process waters. A second group of studies dealt with the adsorption of Al (Nierop et al., 2002), Sb (Araki et al., 2009), Ge (Pokorvsky et al., 2014), Mg (Jolstera et al., 2012), Mo (Afkhami and Norooz-Asl, 2009), V (Brinza et al., 2008) and W (Kashiwabara et al., 2013) onto ferrihydrite ($Fe^{3+}{}_{10}O_{14}(OH)_2$), maghemite ($\gamma$-$Fe_2O_3$), magnetite ($Fe_3O_4$) or goethite ($\alpha$-FeOOH). A third group of papers investigated the incorporation of Al (Cismasu et al., 2012), Ga (Xu et al., 2007), Ge (Liang et al., 2008), In (Chou et al., 2009), Nd (Nagano et al., 1999) and Nb (Oliveira et al., 2009) in the (crystal) structure of ferrihydrite, goethite, hematite (α-Fe_2O_3), or amorphous iron hydroxides. A fourth process is co-precipitation of separate phases like beryllium hydroxide ($Be(OH)_2$) (Burguera et al., 2000) and birnessite ($MnO_2 \cdot H_2O$) (Dietrich and Jacob, 1996) together with ferrihydrite and/or other iron hydroxides.

Conspicuously, most of these studies follow an experimental approach, but are rather limited to fundamental mineralogical and/or hydrogeochemical studies and do not aim for metal recovery from waste waters, apart from one study from the 1970s (Case, 1974). Consequently, this study exceeds the state of the science both with respect to the process engineering approach (Ferrodecont process) and the range of investigated elements (to our knowledge first study on Ta fixation using iron or iron compounds) and with respect to the applied character of the research.

2. Material and methods

2.1. Batch experiments with synthetic solutions

Synthetic solutions ($V = 1$ L) with a desired concentration of 50 mg/L were produced for each critical metal by dissolving standard chemicals in deionized water. The pH was measured after preparation and the concentrations of individual elements in the initial sample were verified according to ÖNORM EN ISO 17294-2 by using inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500 cx). These solutions were mixed in a 1:1 ratio with ZVI (voestalpine Stahl Donawitz AG, austenite + cementite + magnetite + graphite + ledeburite, 4.3 wt% C). The mixtures were shaken in glass bottles ($V = 2$ L) in an overhead shaker for 24 h. Afterwards the suspension was screened at a mesh size of 2 mm to recover the ZVI. The reduction, adsorption and precipitation processes and the subsequent abrasion of the reaction products during the experiment yielded a fine-grained metal concentrate which was separated from the residual solution using double filtration ($d_1 = 2$ μm blue ribbon filter, $d_2 = 0.45$ μm cellulose nitrate filter) with a water jet pump. All fractions were dried and weighed. Critical metal concentrations in the filtrates were analysed by using ICP-MS as described above. Due to incomplete dissolution of standard materials in deionized waters partial deviations from ideal concentrations were observed. Thus, only the truly dissolved concentrations were used for comparison of individual experiments. Concentrations were normalized to the true initial concentration, c_0 and the removal efficiency was calculated according to equation (1):

$$R = \Bigg(1 - \bigg(\frac{c}{c_0}\bigg) \times 100\ [\%] \qquad (1)$$

Based on the results of the initial set of experiments described above and on a survey about the availability of industrial waste waters containing critical elements in Austria, Mo, V, Nb, Co, Ni and Nd were selected for further experiments with synthetic solutions. Firstly, the reaction kinetics was investigated by varying the contact time between the aqueous solutions and the ZVI. The experimental setup was similar as for the first set of experiments, but sampling occurred by syringes equipped with a 0.45 µm syringe filter after 1, 5, 15, 30, 60, 120 and 180 min. Secondly, the impact of pH was investigated by preparing three identical synthetic solutions of the six above mentioned elements. The pH was adjusted to 4, 7 and 10, respectively, by using sodium hydroxide (NaOH) and hydrochloric acid (HCl) as required. Thirdly, the effect of changing the solid to liquid ratio on the removal of critical metals was investigated by a new synthesis of the above mentioned aqueous solutions. The amount of added ZVI was changed to 1000 g/L, 200 g/L and 40. Due to the observed rapid decrease of the removal efficiency a second set of experiments by using 1000 g/L, 500 g/L, 250 g/L of ZVI was carried out. Finally, a set of five experiments using a Mo-containing solution (pH 3, solid to liquid ratio of 1:1) was conducted to validate the reproducibility of the results.

2.2. Batch experiments with industrial waste waters

Waste waters from five different companies (A, B, C, D, E) were selected based on a survey about the accessibility and economic relevance of individual waste water streams. The experimental setup was identical to the one used during the first sequence with synthetic solutions (chapter 2.1); however, a shorter reaction time period of 1 h was chosen.

The waste water of company A had an original pH of 10. In addition to treating the water at the original pH, it was also adjusted to pH 4, 7 and 13 prior to treatment. Two waste waters from company B (labelled B1 (original pH 2) and B2 (original pH 9) were also adjusted to two additional pH values (4 & 7). Additional experiments with B1 and B2 were conducted by using a citric acid buffer (for pH 4) and a phosphate buffer (for pH 7). For the experiments with the citric acid buffer, 10.75 g water-free citric acid and 2.57 g sodium chloride (NaCl) were dissolved in 68 mL 1 M NaOH and diluted with aqua dest. to a volume of 1 L. For the experiments with the phosphate buffer 3.52 g potassium dihydrogen phosphate (KH_2PO_4) and 7.26 g sodium hydrogen phosphate (Na_2HPO_4) · $2H_2O$ were dissolved in 1 L aqua dest. The amount of buffer added to the experimental solution of 1 L was varied (10 mL, 100 mL) for the experiments with both buffers. One waste water from company C was used for batch experiments. It was characterised by its significantly high In content. Company D provided an HF-containing industrial waste water (pH 0.3) with increased concentrations of dissolved Zn, Mo, Sb, cerium (Ce) and In which was used for the experiments. To investigate the effect of partial neutralization, the sample was treated at the original pH and at pH 4. Company E provided two Ni-containing waste waters E1 (original pH 5, high Ni concentration) and E2 (original pH 6, low Ni concentration). Besides the experiments at the original pH, the effect of pH adjustment to pH 7 and 4, on Ni removal was studied.

2.3. Fluidized bed reactor (FBR) experiments with industrial waste waters

Pilot-scale experiments were conducted by using the Ferrodecont process, where fluidized bed reactors (FBR), filled with ZVI granules are used (Höllen et al., 2014). The industrial waste water is pumped into the reactor from the bottom to the top where it interacts with the ZVI granules. After leaving the reactor, the water including the abrasion products are collected and pumped into the reactor again, creating a closed circle. The circulating suspension was sampled via a syringe and separated from the solution via filtration at 0.45 µm after distinct reaction times. The same waste waters which were used for the batch experiments and additional seven waste waters from company C, were selected for FBR experiments. To differentiate between the effect of ZVI and of pH-induced precipitation, sample C4 was chosen for additional experiments. After 3 h of treatment, the pH was raised to pH 10. Additionally, it was set to pH 13 without prior treatment.

2.4. Characterisation of metal concentrates

Chemical analyses of the obtained solids (abrasion products) were conducted according to ÖNORM EN ISO 17294-2 by using an ICP-MS system (Agilent 7500 cx). Prior to analyses, the solids were digested in aqua regia according to ÖNORM EN 13657. Furthermore the fraction >2 mm of the FBR experiments with samples B1, B2, C7 and D were checked for their critical metal content. A selected metal concentrate (2 µm < d < 2 mm, obtained from an experiment with a synthetic Co-containing solution) was investigated by X-ray diffraction (XRD, Pro PANalytical X'Pert Pro, operated with Co-Kα radiation at 40 mA, 45 kV and sample rotation; data were collected in a 2θ angle range between 4° and 110° and an increment of 0.02°). Raman spectroscopy (Jobin Yvon (Horiba) LabRAM, Nd-YAG laser, 532 nm) was applied to this sample to determine its mineralogical composition. Additionally, this sample as well as metal concentrates obtained from industrial waste waters C5 and C6 from FBR experiments were characterised by electron microprobe analyses (EMPA) in element mapping mode with an accelerating voltage of 15 kV and a beam current of 10 nA. For comparison reasons, ZVI granules were exposed to air and to pure water, respectively to study the corrosion of ZVI without the influence of the additionally dissolved ions from synthetic solutions and industrial waste waters.

3. Results and discussion

3.1. Batch experiments with synthetic solutions

Experimental results (Fig. 1) show that more than 98% of dissolved Ge (pH 4.1), Be (pH 4.3), Sb (pH 7.5), Al (pH 3.9) Zn (pH 3.5), Cr (pH 5.4), W (pH 9.2), Ni (pH 6.9), V (pH 4.2), Co (pH 5.8), Ta (pH

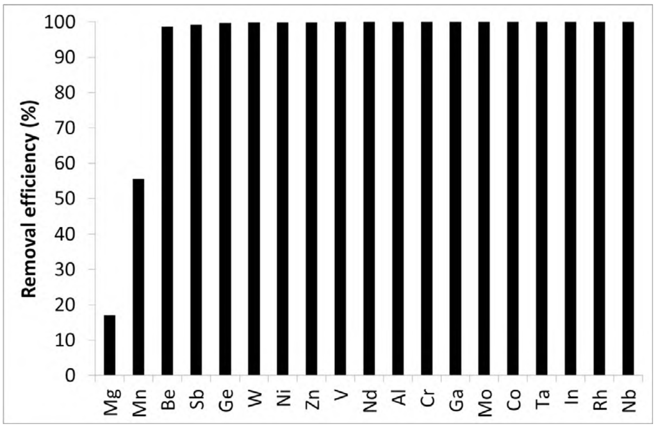

Fig. 1. Removal efficiencies of (potential) critical metals from synthetic solutions after 24 h using ZVI in an overhead shaker.

3.2) and Rh (pH 4.2) were removed from the solution. Concentrations of In (pH 3.8; <0.001 mg/L), Nd (pH 6.1; <0.02 mg/L), Mo (pH 2.9; <0.01 mg/L), Nb (pH 1.8; <0.0005 mg/L) and Ga (pH 3.2; <0.01 mg/L) were below the detection limit in the filtrate after the experiments, leading to a removal efficiency of more than 99%. Only in case of Mg (pH 7.7) and Mn (pH 6.7) the removal efficiencies were below 60%. In case of Mg this might be explained by the formation of aqueous magnesium carbonate ($MgCO_3$) complexes which shift the activity of free Mg^{2+} ions (von Breymann et al., 1990)

Despite larger variations between experiments with individual elements, reaction kinetics experiments indicate that most of the fixation is already completed after 1 h (Fig. 2). Vanadium is already removed from solution after the first few minutes of treatment whereas the process lasts several hours in case of Ni and Co. This can be explained by the high affinity of V to iron hydroxides which has already been modelled for V leaching from steel slags (Höllen et al., 2017).

Experiments conducted at different pH (Fig. 3) indicate that Mo and V are preferentially removed at pH 4, whereas Co is preferentially fixed at pH 10. Molybdenum and V are present as negatively charged oxyanions, e.g., vanadate (VO_4^{3-}) and molybdate (MoO_4^{2-}), which are adsorbed at a pH below the point of zero charge of iron hydroxides (~pH 9), which are suggested to have formed by oxidative dissolution of ZVI (Noubactep, 2010). Contrary, Co is present in the solution as Co^{2+} cations which are preferentially adsorbed at alkaline pH when the surface charge becomes negative. Alternatively, precipitation of cobalt hydroxide ($Co(OH)_2$) may also take place.

Experiments with varying solid:liquid ratios (Fig. 4A) clearly indicate that the optimum ratio is 1:1 (1000 g/L ZVI), although lower ratios might be sufficient to achieve the desired efficiency for certain elements. Experiments to check the reproducibility of the results showed that the statistic deviation of the experiments is relatively large (Fig. 4B). Main factors for these differences are the synthesis of the aqueous solutions because the initial concentration already revealed large variations (±20%) and the strong impact of random effects in the experiments themselves such as the amount of ZVI which is being oxidized within the reactor etc. (removal efficiency is between 80 and 90%).

3.2. Batch experiments with industrial waste waters

In general, batch experiments with industrial waste waters (Fig. 5) confirmed the principal suitability of ZVI to remove critical metals from aqueous solutions which was shown using synthetic solutions (Fig. 1). However, in practical operation cations and anions are both present in industrial wastewater and will behave differently, i.e. are not removed simultaneously. However, this selectivity of the process can also be a benefit for subsequent recycling.

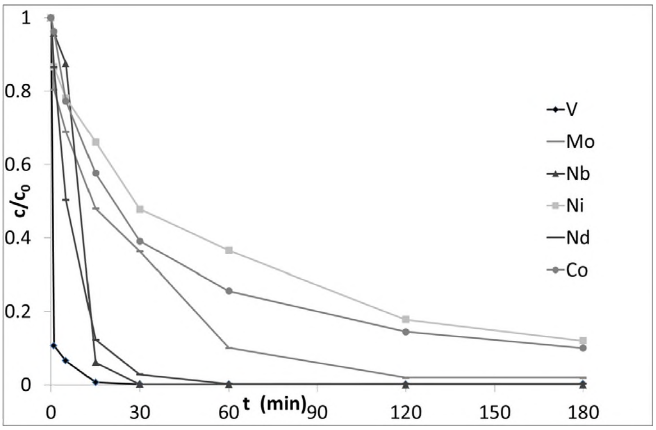

Fig. 2. Fixation kinetics of selected critical metals from synthetic solutions onto ZVI.

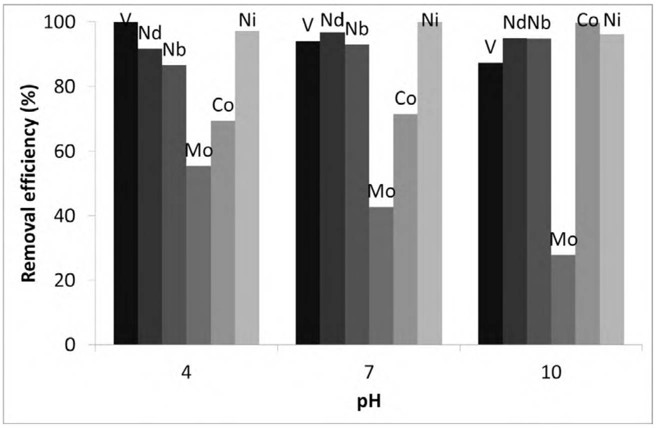

Fig. 3. Effect of pH on critical metal removal from synthetic solutions by ZVI.

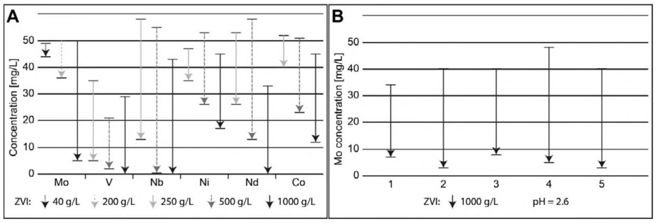

Fig. 4. A: Effect of solid:liquid ratio (given as ZVI concentration in experimental suspension) on removal of Mo, V, Nb, Ni, Nd and Co from synthetic solutions (arrows mark the concentration decrease during the experiment). B: Decrease of Mo concentration in a set of five replicate experiments with a synthetic solution.

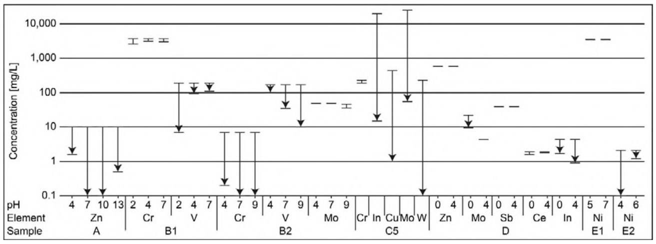

Fig. 5. Removal of critical elements from selected industrial waste waters (A, B1, B2, C5, D, E1 and E2) in batch experiments.

This might be one explanation why some differences were found compared to the experiments with synthetic solutions. Batch experiments with a Zn-containing waste water from company A yielded a removal efficiency for Zn of mostly more than 90%. Batch experiments with a weakly mineralized industrial waste water (B2) yielded a removal of 99% of dissolved Cr and about 75% of dissolved V over a broad pH range, whereas from a highly mineralized industrial waste water (B1) these efficiencies could not be reached. In the experiment with the industrial waste water C5 more than 99% of dissolved In, Cu, Mo and W could be removed, whereas Cr remained in the solution.

Despite addition of pH buffers during additional experiments even above the stoichiometrically required amount had a limited effect on pH stability. This may be due to consumption of the buffer by other reactants or due to the inhibition by other components.

3.3. *Fluidized bed reactor (FBR) experiments with industrial waste waters*

Generally, FBR experiments with industrial waste waters (Fig. 6) confirmed the results of batch experiments. However, some differences occur in individual experiments. Contrary to the experiments in the batch reactor (Fig. 5) only little Zn could be removed from waste water A during the FBR experiments, which was additionally partly remobilized in the course of the experiment. In contrast to experiments with batch reactors, eight different industrial waste waters of company C were selected for FBR experiments. In some of the samples (e.g., C5) more than 80% of dissolved W and Mo could be recovered, whereas for other samples (e.g., C2, see appendix) the dissolved concentrations of W and Mo remained constant. In those samples, where In and Cu were present (C5, C6, see appendix), they could be removed to more than 90%. Experiments with sample C4 where precipitation was induced after 3 h treatment or instead of the treatment with ZVI (see appendix) indicate that classical hydroxide precipitation is not a suitable process for Mo removal and also has a bad performance for W removal whereas both metals can be recovered by ZVI.

Although experiments in the batch reactor did not yield a removal of significant amounts of critical metals from the industrial waste water of company D, the FBR showed some decrease in the concentrations of dissolved Mo and In which have to be assessed critically due to the large variation of the results (Fig. 4B). In case of the industrial waste waters from company E, FBR experiments confirmed the results of the batch experiments according to which more than 90% of dissolved Ni were removed from the lower concentrated sample E2 whereas no removal occurred in case of the higher concentrated sample E1 (see appendix). This suggests that the adsorption capacity was already exhausted in the second case.

3.4. *Characterisation of metal concentrates*

Corrosion of ZVI, abrasion of the corrosion products and double separation of this fine-grained material at 0.45 μm and 2 μm yields metal concentrates in which critical metals are enriched compared to the treated aqueous solution. The chemical and mineralogical composition of individual metal concentrates from single experiments is described here in detail.

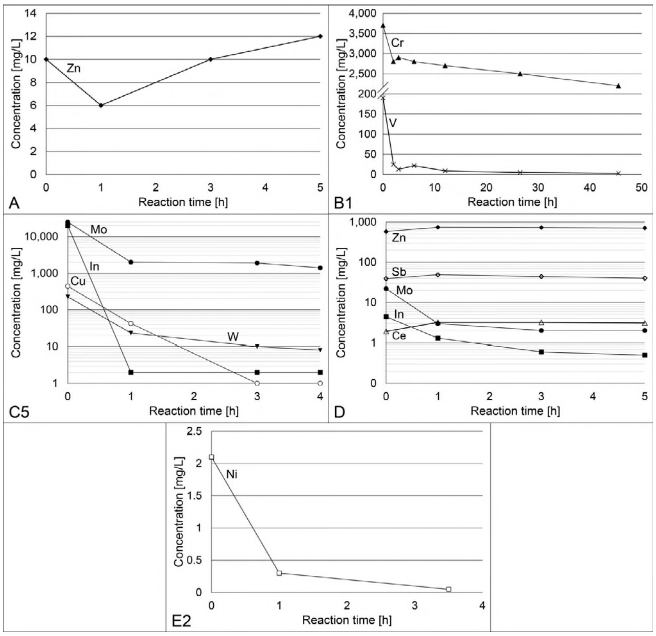

Fig. 6. Removal of critical metals from selected industrial waste waters (A, B1, C5, D, E2) using the FBR.

The mass fraction of the produced metal concentrate and its grain size distribution varied for individual experiments. In average, about 0.4% of the initial mass of ZVI were transferred into the fine-grained metal concentrate (<2 mm) with 0.07% being <2 μm. According to the diverging amount of particles <2 μm, filtrations times varied between few minutes up to several hours. The metal concentrates were characterised by critical metal concentrations of about 1 wt% which was both calculated from the decrease in dissolved concentrations and measured by chemical analyses of digested solids. This range is similar to that observed in natural ore deposits of several of these elements. The total removal of critical metals was about 50 mg critical metal per kg ZVI. The operational life of the ZVI depends strongly on pH and was not determined during this study. However, in a previous study (Müller et al., 2014), about 50% of ZVI were consumed within one year continuous operation and had to be replaced. Variations in the content of critical elements in the metal concentrate were rather due to a different amount of fine-grained material formed in the experiment than due to different removal efficiencies of critical metals from the solution. Another reason for the variations is the incomplete collection of the produced metal concentrates due to its fine grain size and its attachment to the ZVI. This is especially valid for the refractory metals Ta, Nb and W. With concentrations between 500 and 600 mg/kg, Fe is always the main component of the metal concentrates which is in agreement with mineralogical observations below as pure iron(III) hydroxide ($Fe(OH)_3$) contains 52 wt% Fe. Measured concentrations vary for the sub-fractions <2 μm and > 2 μm and are provided in Table 1.

XRD analyses of a selected metal concentrate from an experiment with Co solution showed a mineralogical composition of graphite (α-C), magnetite (Fe_3O_4), lepidocrocite (γ-FeOOH) and goethite (α-FeOOH) whereas no critical metal bearing phases could be identified (Fig. 7). A comparative experiment where ZVI was exposed to air only and the corrosion products were characterised accordingly yielded also the formation of goethite, but not of lepidocrocite. A second comparative experiment where ZVI was exposed to pure water yielded the formation of lepidocrocite, too, which demonstrates that this phase forms during subaquatic corrosion independent from the influence of Co ions (see Fig. 8).

Raman spectroscopy confirmed the presence of lepidocrocite and magnetite and revealed the disordered character of the contained graphite. Comparing the phase assemblage of the metal concentrate after the experiment with the phase composition of the ZVI (chapter 2.1), it can be seen that lepidocrocite and additional magnetite formed during the experiment. This suggests that critical metals are predominantly fixed at or inside these phases. However, the fixation mechanism, i.e., adsorption, precipitation or incorporation, cannot be concluded from these results. Elemental Co distributions obtained from EMPA clearly indicate that Co is only bound to Fe hydroxide phases, but not to graphite.

Batch experiments with the industrial waste waters B1 and B2 yielded metal concentrates with comparable contents of critical metals (in the range of 1 wt%, Fig. 9) like obtained in the experiments with synthetic solutions. FBR experiments with the industrial waste water C5 yielded a metal concentrate with 11 wt% of Mo and 2 wt% of In; the corresponding experiment with the industrial waste water C6 yielded a metal concentrate with 27% of Cu (Fig. 9). However, the In content of the metal concentrate of C5, calculated from solution chemistry, should be even higher, which might be due to the colloidal character resulting in an incomplete sampling.

Table 1
Concentrations of critical metal concentrates produced from synthetic one-element aqueous solutions in batch reactors (in case of two values the first refers to the coarse fraction > 2 mm, the second to the fine fraction <2 mm).

Content in metal concentrates [wt%]																		
In	Nd	Mo	Be	Ta	Rh	Sb	Ga	W	Mg	Co	Al	Ni	Mn	V	Nb	Cr	Ge	Zn
0.98	1.18	1.19	0.53	0.001	0.86	2.96	1.48	0.08	0.25	0.89	4.39	0.74	1.74	3.93	0.09	2.16	0.67	0.14
							1.42		0.66	1.04	3.85	0.91			0.04	2.23	0.04	

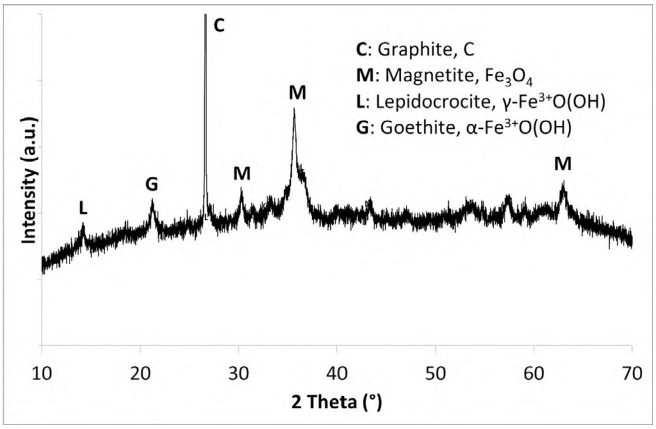

Fig. 7. XRD pattern of a metal concentrate (2 µm < d < 2 mm) obtained from a synthetic Co solution.

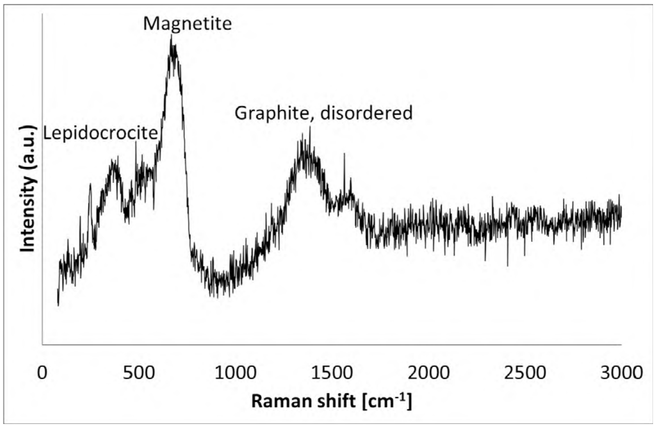

Fig. 8. Raman spectrum of a metal concentrate (2 µm < d < 2 mm) obtained from a synthetic Co solution.

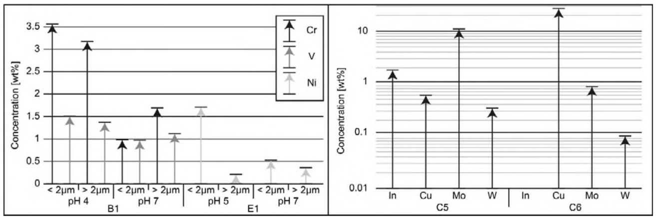

Fig. 9. Critical metal contents in the metal concentrates obtained from batch experiments with industrial waste waters B1 and E1 (left) and FBR experiments with industrial waste waters C5 and C6 (right).

Contrary, batch experiments with the industrial waste water from company D (see appendix) yielded solids with critical metal contents below 1 wt%. The industrial waste waters E1 and E2 were treated at different pH. Solely sample E1, treated at pH yielded metal concentrates with more than 1 wt% Ni (Fig. 9).

Chemical analyses of the recovered ZVI, i.e., the fraction > 2 mm clearly indicated that concentrations of the critical metals in this fraction were always below 0.03 wt% which demonstrates that removed metals are fixed in the abraded corrosion products and are not incorporated in the remaining ZVI. A plausibility check between the contents in the metal concentrates calculated from the decrease in dissolved concentration and those measured directly in the solids shows significant differences in many cases. On the one hand, chemical elements were found in significant concentrations in the solid whose concentration in the solution did not decrease significantly, on the other hand elements whose dissolved concentration decreased significantly were not found in the solid. These inconsistencies might be explained by local precipitates which do not influence bulk solution chemistry or by an incomplete recovery of the partially colloidal precipitate formed during the experiments. They are studied in a follow-up project for better reproducibility of the results.

In contrast to experiments with the synthetic Co solution, the experiments with the industrial waste waters C5 and C6 showed besides ZVI corrosion the formation of specific phases which

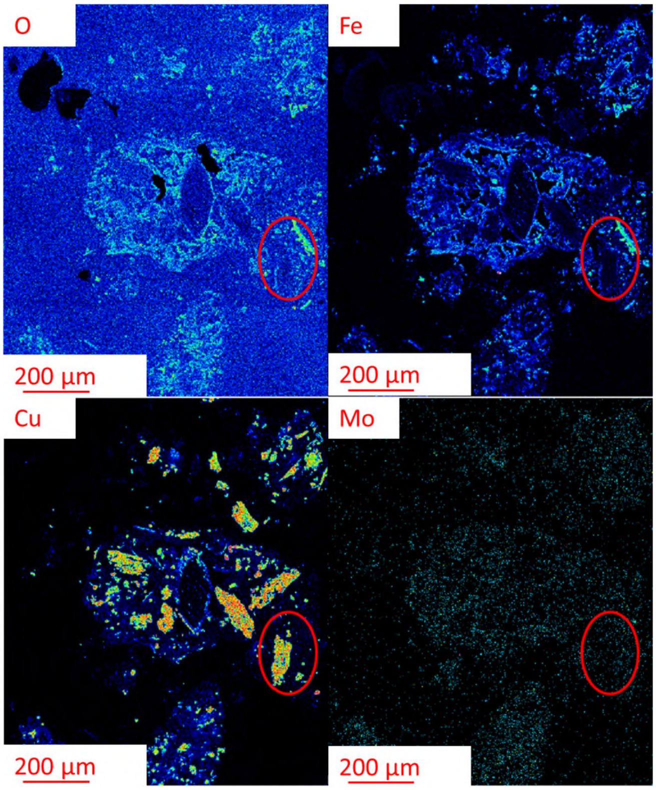

Fig. 10. Elemental distribution of O (top left), Fe (top right), Cu (bottom left) and Mo (bottom right) obtained from FBR treatment of industrial waste water C6: Fe is present as oxide, Cu as metal and Mo rather as metal, too.

incorporate the removed critical metals. This is due to the additional presence of other chemical components which influence dissolution, precipitation, adsorption and desorption equilibria and kinetics and thereby the mobility, fixation, binding form and speciation of critical metals in the process. In the metal concentrate obtained during FBR treatment of the industrial waste water C5 it was shown by EMPA mapping that In is associated with Mo and sulphur (S) and partially with oxygen (O), which suggests the formation of an In-Mo-sulphide or In-Mo-sulphate. Finally, the same analytical approach yielded the proof of the formation of metallic Cu in the metal concentrate obtained during FBR treatment of the industrial waste water C6 (Fig. 10). This finding is highly promising with respect to the economic feasibility of Cu recovery from industrial waste waters using the Ferrodecont process.

4. Conclusions

ZVI was successfully used to remove critical metals from synthetic aqueous solutions using batch reactors and FBRs. Experiments with synthetic solutions could remove more than 99% of most dissolved critical metals. These results are in good agreement with those from experiments with industrial waste waters where mostly between 75 and 90% of dissolved critical metals could be recovered. Experiments with FBR and batch reactors were also in relatively good agreement with each other. Resulting metal concentrates of both synthetic and industrial waste waters consist of iron (hydr)oxides with critical metal contents in the range of about 1 wt%. Metal concentrates obtained from industrial waste waters may contain additional phases like metallic Cu which are highly promising with respect to metal recovery. Further research is conducted in a follow-up project about beneficiation and recycling of the produced metal concentrates. The methods investigated therein include selected inorganic or biological leaching, thermal treatment, ionic liquids and solvent extraction.

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Declarations of interest

None.

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Appendix

Table A1
Overview on experiments with synthetic solutions

	Desired concentration	ZVI concentration	Experimental duration	pH	Element	Chemical used for synthetic solution	Producer	Purity
Experiments at standard conditions	50 mg/L	1000 g/L	24 h	3.9	Al	$Al_2(SO_4)_3 \cdot 16H_2O$	Fluka	p.a.
				4.3	Be	$BeSO_4$	Alfa Aesar	98%
				5.8	Co	$Co(NO_3)_2 \cdot 6H_2O$	Fluka	p.a.
				5.4	Cr	$K_2Cr_2O_7$	Fluka	p.a.
				3.2	Ga	$GaCl_3$	Alfa Aesar	crystalline
				4.1	Ge	ICP standard	Roth	–
				7.7	Mg	$MgCl_2$	Roth	98.5%
				3.8	In	$InCl_3$	Alfa Aesar	crystalline
				6.7	Mn	$MnSO_4 \cdot H_2O$	Fluka	p.a.
				2.9	Mo	$MoCl_3$	Alfa Aesar	99.6%
				1.8	Nb	ICP standard	Roth	–
				6.1	Nd	$NdCl_3$	Alfa Aesar	crystalline
				6.9	Ni	$Ni(NO_3)_2 \cdot 6H_2O$	Fluka	p.a.
				4.2	Rh	$RhCl_3 \cdot 3\ H_2O$	Alfa Aesar	38–45.5% Rh
				7.5	Sb	Sb_2O_3	Merck	p.a.
				3.2	Ta	$TaCl_5$	Alfa Aesar	99.99%
				4.2	V	V_2O_5	Riedel de Haen	purest
				9.2	W	ICP standard	Ultra Sicentific	–
				5.6	Zn	$C_4H_6O_4Zn \cdot 2H_2O$	Fluka	p.a.
Experiments for reaction kinetics	50 mg/L	1000 g/L	1, 5, 15, 30, 60, 120 and 180 min	5.7	Co	$Co(NO_3)_2 \cdot 6H_2O$	Fluka	p.a.
				3.0	Mo	$MoCl_3$	Alfa Aesar	99.6%
				1.8	Nb	ICP standard	Roth	–
				5.4	Nd	$NdCl_3$	Alfa Aesar	crystalline
				5.0	Ni	$Ni(NO_3)_2 \cdot 6H_2O$	Fluka	p.a.
				4.2	V	V_2O_5	Riedel de Haen	purest
Experiments for pH impact	50 mg/L	1000 g/L	1 h	4,7,10	Co	$Co(NO_3)_2 \cdot 6H_2O$	Fluka	p.a.
					Mo	$MoCl_3$	Alfa Aesar	99.6%
					Nb	ICP standard	Roth	–
					Nd	$NdCl_3$	Alfa Aesar	crystalline
					Ni	$Ni(NO_3)_2 \cdot 6H_2O$	Fluka	p.a.
					V	V_2O_5	Riedel de Haen	purest
Experiments for solid: liquid ratio impact	50 mg/L	1000 g/L, 500 g/L, 250 g/L	1 h	5.7	Co	$Co(NO_3)_2 \cdot 6H_2O$	Fluka	p.a.
		1000 g/L, 200 g/L, 40 g/L		n.a.	Mo	$MoCl_3$	Alfa Aesar	99.6%
		1000 g/L, 500 g/L, 250 g/L		1.8	Nb	ICP standard	Roth	–
		1000 g/L, 500 g/L, 250 g/L		5.3–5.4	Nd	$NdCl_3$	Alfa Aesar	crystalline
		1000 g/L, 500 g/L, 250 g/L		5.0–5.1	Ni	$Ni(NO_3)_2 \cdot 6H_2O$	Fluka	p.a.
		1000 g/L, 500 g/L, 250 g/L		4.2	V	V_2O_5	Riedel de Haen	purest

(*continued on next page*)

Table A1 (*continued*)

	Desired concen-tration	ZVI concen-tration	Experimen-tal duration	pH	Ele-ment	Chemical used for synthetic solution	Pro-ducer	Purity
Experiments for reprodu-cibility	50 mg/L	1000 g/L	1 h	2.6	Mo	$MoCl_3$	Alfa Aesar	99.6%

Table A2
Determination of the demand of ZVI for critical metal removal from synthetic solutions

Synthetic one −element starting solution	Amount of ZVI [g/L], reaction time [min] and concentration [mg/L]									
	40 g/L		200 g/L		250 g/L		500 g/L		1000 g/L	
	0	60	0	60	0	60	0	60	0	60
V					35	5	21	2	29	0.04
Mo	49	44	50	36					50	5
Nb					58	13	55	0.4	43	0,01
Ni					47	35	53	26	45	17
Nd					53	26	58	13	33	<0.1
Co					52	40	51	23	45	12

Table A3
Determination of the reproducibility of experimental results

Synthetic one-element starting solution	Reaction time [min], number of experiment and concentration [mg/L]									
	1		2		3		4		5	
	0	60	0	60	0	60	0	60	0	60
Mo	34	7	40	3	40	8	48	5	40	3

Table A4
Zn removal from an industrial waste water of company A in a batch reactor

Element	Sample and concentration [mg/L]				
	A	Filtrate pH 4	Filtrate pH 7	Filtrate pH 10	Filtrate pH 13
Zn	10	1,6	0.1	<0.1	0,5

Table A5
Cr, V and Mo removal from two industrial waste waters (B1, B2) of company B in a batch reactor

Element	Sample and concentration [mg/L]							
	B1	Filtrate pH 2	Filtrate pH 4	Filtrate pH 7	B2	Filtrate pH 4	Filtrate pH 7	Filtrate pH 9
Cr	3700	2600	3100	3000	7.0	0.2	0.1	0.1
V	190	7	93	110	170	100	35	10
Mo	<1	<1	<1	<1	46	49	49	36

Table A6
Influence of buffer concentration of the stability of pH during treatment of industrial waste waters B1 and B2 (italics: outlier without explanation) in a batch reactor

Para-meter	Sample and pH							
	B1, pH 4	Filtrate pH 4, without buffer	Filtrate pH 4, with 10 mL buffer	Filtrate pH 4, with 100 mL buffer	B1 pH 7	Filtrate pH 7, without buffer	Filtrate pH 7, with 10 mL buffer	Filtrate pH 7, with 100 mL buffer
pH	4.0	5.6	*6.8*	5.2	7.0	7.4	7.7	7.3
	B2 pH 4	Filtrate pH 4, without buffer	Filtrate pH 4, with 10 mL buffer	Filtrate pH 4, with 100 mL buffer	B2 pH 7	Filtrate pH 7, without buffer	Filtrate pH 7, with 10 mL buffer	Filtrate pH 7, with 100 mL buffer
pH	4.1	6.9	6.3	6.1	7.0	8.2	7.9	7.3

Table A7
Recovery of In, Cu, Mo, W and Cr from an industrial waste water C5 in a batch reactor

Element	Sample and concentration [mg/L]	
	C5	Filtrate
Cr	230	190
In	20 000	15
Cu	440	1
Mo	25 000	55
W	230	<1

Table A8
Removal of critical metals from an industrial waste water of company D in a batch reactor

Element	Sample and concentration [mg/L]		
	D	Filtrate pH 0	Filtrate pH 4
Zn	580	610	610
Mo	22	9.5	4.3
Sb	39	42	40
Ce	1.9	1.6	1.8
In	4.4	1.7	0.9

Table A9
Removal of Ni from two industrial waste waters E1 and E2 in a batch reactor

Element	Sample and concentration [mg/L]					
	E1	Filtrate pH 5	Filtrate pH 7	E2	Filtrate pH 4	Filtrate pH 6
Ni	3500	4400	3500	2.1	0.1	1.2

Table A10
Removal of Zn from an industrial waste water of company A using the FBR

Element	Reaction time [h] and concentration [mg/L]			
	0	1	3	5
Zn	10	6	10	12

Table A11
Removal of Cr, V and Mo from two industrial waste waters of company B using the FBR

Element	Sample, reaction time [h] and concentration [mg/L]									
	B1							B2		
	0	2	3	6	12	26,5	45,5	0	1	3
Cr	3700	2800	2900	2800	2700	2500	2200	7.0	2.3	0.8
V	190	25	13	22	9	5	3	170	140	140
Mo	<1	<1	<1	<1	<1	<1	<1	46	45	46

Table A12
Removal of critical metals from eight industrial waste waters from company C using the FBR

Element	Sample, reaction time [h] and concentration [mg/L]								
	C1			C2			C3		
	0	1	3	0	1	3	0	1	3
Mo	55	31	48	37	30	33	28	8	3
W	82	21	31	7	6	4	2.5	1.4	1.0
Co							20	26	19

Element	Sample, reaction time [h] and concentration [mg/L]						
	C4						
	0	1	3	5	12	3 + precipitation at pH 10	0 + precipitation at pH 13
Mo	160	76	110	100	86	12	180
W	39	9	14	15	12	4	15

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Table A12 (*continued*)

Element	Sample, reaction time [h] and concentration [mg/L]						
	C4						
	0	1	3	5	12	3 + precipitation at pH 10	0 + precipitation at pH 13
Element	**Sample, reaction time [h] and concentration [mg/L]**						
	C5				**C6**		
	0	**1**	**3**	**4**	**0**	**1**	**3**
In	20 000	2	2	2	11	1	0.3
Cu	440	42	1	1	580	11	23
Mo	25 000	2000	1900	1400	220	180	170
W	230	23	10	8	18	3	3
Element	**Sample, reaction time [h] and concentration [mg/L]**						
	C7				**C8**		
	0	**1**	**3**	**6**	**0**	**1**	**3**
Mo	4	5	2	1	3.7	0.7	0.2
W	2200	780	280	120	2300	440	92

Table A13
Removal of critical metals from an industrial waste water from company D using the FBR

Element	Reaction time [h] and concentration [mg/L]			
	0	1	3	5
Zn	580	740	730	710
Mo	22	3	2	2
Sb	39	49	44	40
Ce	1.9	3.2	3.2	3.1
In	4.4	1.3	0.6	0.5

Table A14
Removal of Ni from from two industrial waste waters E1 and E2 from company E using the FBR

Element	Reaction time [h] and concentration [mg/L]					
	E1			E2		
	0	0,7	2	0	1	3,5
Ni	3500	4200	4300	2.1	0.3	0.05

Table A15
Concentrations of critical metal concentrates produced from synthetic aqueous solutions in batch reactors (in case of two values the first refers to the coarse fraction > 2 mm, the second to the fine fraction < 2 mm)

Content in metal concentrates [wt%]																		
In	Nd	Mo	Be	Ta	Rh	Sb	Ga	W	Mg	Co	Al	Ni	Mn	V	Nb	Cr	Ge	Zn
0.98	1.18	1.19	0.53	0.001	0.86	2.96	1.48	0.08	0.25	0.89	4.39	0.74	1.74	3.93	0.09	2.16	0.67	0.14
							1.42		0.66	1.04	3.85	0.91			0.04	2.23	0.04	

Table A16
Critical metal contents in the metal concentrates obtained from batch experiments with industrial waste waters B1 and B2

Element	Waste water, pH, grain size fraction and critical metal content in the metal concentrate [wt%]							
	B1				B2			
	pH 4		pH 7		pH 4		pH 7	
	<2 μm	>2 μm	<2 μm	>2 μm	<2 μm	>2 μm	<2 μm	>2 μm
Cr	3.56	3.17	0.98	1.69	0.06	0.07	0.46	0.37
V	1.51	1.37	0.97	1.12	0.36	0.31	3.17	2.94

Table A17
Critical metal contents in the metal concentrates obtained from FBR experiments with industrial waste waters of company C

Element	Waste water and critical metal content in the metal concentrate [wt%]		
	C2	C5	C6
In	<0.01	1.81	<0.01
Cu	0.04	0.60	27.0
Mo	0.09	11.0	0.88
W	0.30	0.34	0.10
Co	3.45	<0.01	<0.01

Table A18
Critical metal contents in the metal concentrates obtained from batch experiments with an industrial waste water of company D

Element	pH, grain size and critical metal content in the metal concentrate [wt%]			
	pH 0		pH 4	
	<2 μm	>2 μm	<2 μm	>2 μm
Zn	0.74	<0.16	0.26	0.16
Mo	0.02	0.03	0.02	0.01
Sb	0.09	0.10	0.07	0.07
Ce	<0.01	<0.01	0.03	0.03
In	0.01	<0.01	0.01	<0.01

Table A19
Critical metal contents in the metal concentrates obtained from the batch experiments with industrial waste waters from company E

Element	Waste water, pH, grain size and critical metal content in the metal concentrate [wt%]							
	E1				E2			
	pH 5		pH 7		pH 4		pH 6	
	<2 μm	>2 μm	<2 μm	>2 μm	<2 μm	>2 μm	<2 μm	>2 μm
Ni	1.71	0.21	0.53	0.36	0.13	0.09	0.12	0.12

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