

## Experimental determination of process parameters for mine water treatment and permissible utilization of the iron-rich residues

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### Abstract

Addressing the objective of designing and sizing the technological steps of a mine water treatment plant to be built, the procedures and major results of determining relevant process parameters from experimental process simulation are described in this work. This approach includes generation of expectations from thermodynamic modeling, pre-experiments for designing and sizing of experimental setups, estimation of upscaling factors and task-specific reactor experiments along the process chain of mine water oxidation, neutralization, flocculation, sedimentation, dewatering and re-use of residues. By testing different types and doses of coagulants, coagulation aids, and orders of dosing, a new treatment sequence was found to provide the best iron elimination result. Based on the process parameters, the technical components of the treatment plant and the volume / mass of residues were sized and a permissible alternative for re-use of the iron hydroxide loaded residues (EHR) proposed.

Because emplacement of such alkalinity loaded residues within mining dumps appears licensable and is already practiced at a lignite mine nearby, a series of reactor experiments was performed to investigate the interaction and fate of EHR embedded within tertiary overburden sands for scenarios of simulated groundwater recharge and rise. The results show that the carbonate alkalinity in EHR effectively buffered acidity stored or generated by pyrite weathering in the overburden sands, thereby thwarting acid dissolution of EHR. The output of acidity, sulfate, Fe<sup>2+</sup>, and heavy metal ions from test reactors was lower than from EHR-free control reactors, and lowest when mixing EHR with the overburden substrate. The overall results neither indicate chemical dissolution of EHR nor suggest favorable conditions for microbial iron reduction.

Key words: Process simulation, mine water treatment, residue utilization, groundwater recharge / rise

### Introduction

Mine waters usually require treatment to comply with regulatory threshold values for discharge into public streams. For the expansion of an open-cast lignite mine, a new mine water treatment plant had to be planned. The task was to design and size the technological treatment steps to fulfil the official thresholds for discharge quality: pH 6.5–8.5, dissolved oxygen (DO) >5 mg/L, total suspended solids (TSS) <30 mg/L, total iron (Fe-tot) <1.5 mg/L, dissolved iron (Fe-diss) <0.2 mg/L. This contribution demonstrates a feasible approach of determining critical parameters from experimental bench-scale and mesoscale process simulation to select ideal additives and arrange and size the treatment steps. A second objective was to propose alternatives for permissible utilization of treatment residues loaded with iron oxy-hydroxides (termed EHR). Based on authorized practice at an operating treatment plant, lab experiments were designed to investigate interactions and fate of EHR buried together with tertiary overburden sands in deep mine dumps for the scenarios of groundwater recharge and rise.

### Methods

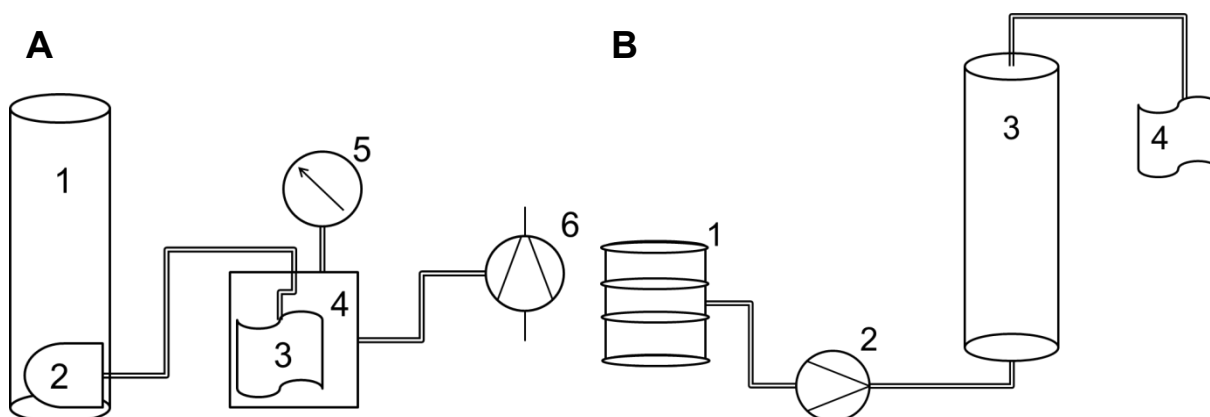
To address the first objective, a step-wise process simulation workflow was developed including

- Comparison of actual mine water quality data with forecast values,
- Characterization of relevant mine waters, selection of a *typical* and a *worst-case* test water;
- Pretests and bench-scale simulation experiments for single treatment steps (oxidation, neutralization, flocculation, sedimentation);
- Combination of treatment steps in a mesoscale experiment, collection of EHR for dewatering;
- Refinement of critical treatment steps, estimation of an upscaling factor;

- Gross design and sizing of treatment process technology.

This contribution can only illustrate selected steps of this workflow to meet space limitations.

Based on the proposed licensable utilization of EHR, samples of tertiary overburden sand, deposited EHR, and deep groundwater were collected from the Schleenhain lignite mine to study the second objective. Soil physical and chemical properties and reactivity of test substrates were determined to size the load of substrates and arrangement of layers in the experimental reactors, operated according to intermittent-flow batch reactors by setups shown in Figure 1. This means one pore volume of test substrate was exchanged with test water at a flow rate of up to 1 m/d, followed by a 24 h rest to enable equilibrium with the hydraulically less active pore space. By applying eleven of such exchange-and-rest cycles during the experiment, and assuming a porewater flow rate of 0.2 m/d as an upper bound through a 30 m thick mine dump, the experiments would mimic fundamental chemical reactions over a period of at least 5 years. The simulation of slower microbial reactions was neglected for this test phase because organic carbon contents of the test substrates were very low. The collected reactor effluents were analyzed for pH, redox potential, acidity, alkalinity, inorganic (DIC) and organic carbon (DOC), sulfate, iron, and other ionic components. Total alkalinity and sulfur were balanced considering input, output, and change of reactor pools.



**Figure 1** Sketch of experimental setups for simulation of (A) groundwater recharge: Open-top column filled with test substrate (1), vacuum porewater sampler (2) connected with Tedlar bag (3) stored in a pressure vessel (4) at which a vacuum pump (6) can induce low-pressure of 0.1 bar checkable by a gauge (5); and (B) groundwater rise: Groundwater stored in a stainless steel vessel (1) is transferred by peristaltic pump (2) into a column filled with test substrate (3), and the effluent is captured in a Tedlar bag (4).

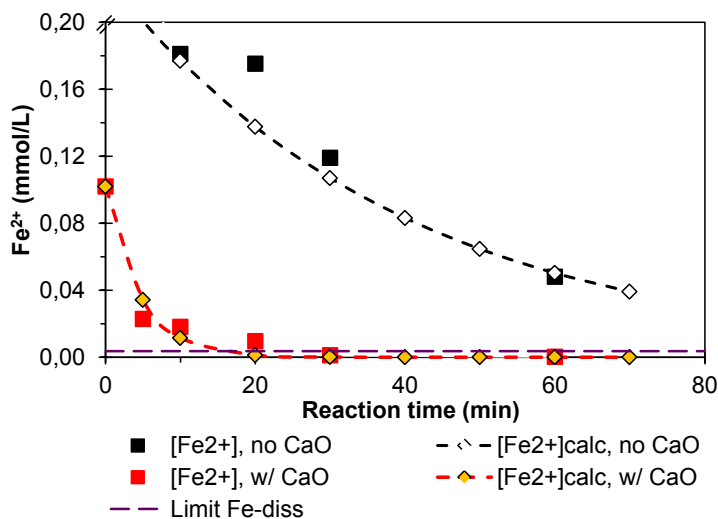
Only standardized and accredited analytical methods were applied, and all results were documented in lab reports. Open-source PhreeqC code with implemented database was used for thermodynamic process simulation.

### Results of Treatment Process Simulation

**Neutralization potential.** In-situ acidity, alkalinity, and their change when reaching air equilibrium after complete oxidation and CO<sub>2</sub> exchange, were calculated with PhreeqC by stepwise precipitation of thermodynamically supersaturated mineral phases. Contrary to some other mining areas, intrinsic alkalinity of all test waters exceeded the acidity generated by hydrolysis of oxidized Fe(II) and Mn(II). Hence, a neutralizing step was unnecessary. Calcite precipitation was predicted to stabilize pH<sub>eq</sub> of 7.8–8.0, while gypsum remained undersaturated. Batch titration experiments confirmed these results.

**Oxidation kinetics and lime supply.** Without technical aeration, the Fe(II) oxidation rate revealed  $1 \cdot 10^{-6}$  M/h. Aeration with a gas flow of 17 L/h increased this linear rate to  $1.8 \cdot 10^{-4}$  M/h. However, a 50 g/m<sup>3</sup> supply of slaked quicklime (CaO) led the Fe<sup>2+</sup> concentration exponentially decrease below the target value within 30 min, mainly due to increased pH (Fig. 2). Assuming initially anoxic mine water with 10 to 50 mg/L Fe(II) and volumetric flow of 120 m<sup>3</sup>/min, an air demand of 0.019–0.096 m<sup>3</sup> per 1 m<sup>3</sup> of raw water was calculated. To meet this demand, we proposed an appropriate number of spiral aerators to be arranged in the front part of the water processing channel. To determine the optimum quicklime demand

for pH adjustment, the applicable dose range was first estimated by PhreeqC. Then, a series of individual batch experiments was performed with supply of 0, 6.1, 30.7, and 92 g/m<sup>3</sup> of slaked quicklime to the test water, which was aerated for 0, 5, 10, 20, 30, 60, and 90 min by a gas flow of 12 L/(L•h). After each time, the corresponding batch water was analyzed with respect to pH, O<sub>2</sub>, Fe<sup>2+</sup>, Ca<sup>2+</sup>, and TIC. According to the results (not shown here), a quicklime dose of roughly 60 g/m<sup>3</sup> would ensure compliance with the official Fe-diss threshold value within 30 min. One of the test waters showed that this dose can even be reduced if the mine water contains sufficient particles with catalytically active surfaces.



**Figure 2** Oxidation kinetics of Fe<sup>2+</sup> in the absence and presence of slaked quicklime (CaO) for test water #2. Squares show analyzed data, curves are calculated from a kinetic rate law according to Singer & Stumm (1970).

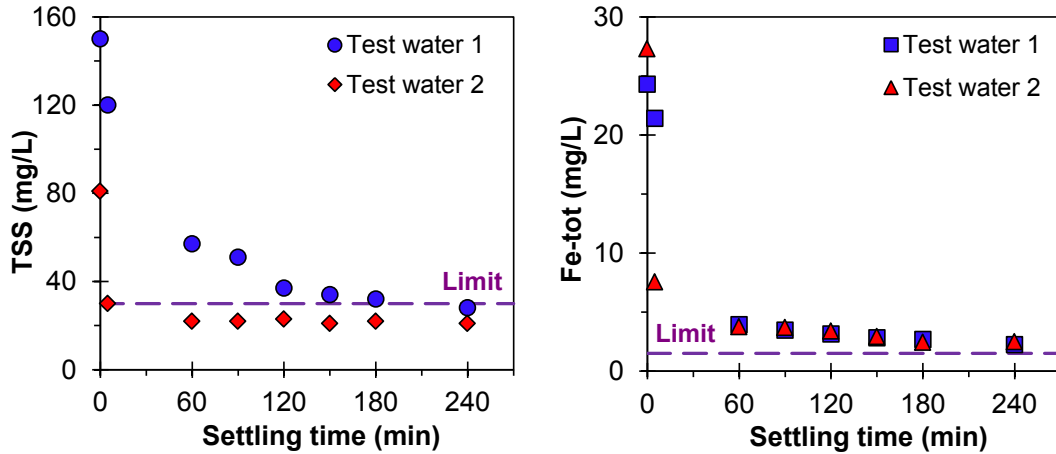
*Coagulation and sedimentation.* The aim of this treatment step was to select the most effective coagulation aid among three high-molecular anionic products that differed with respect to charge density. Initial volumes of test water were oxidized in the presence or absence of slaked quicklime. After splitting the pre-treated waters into forty 1 L glass cylinders, various doses of coagulation aid were added. Coagulation effectivity was determined by comparing the settling rates and the supernatant Fe-tot concentrations as a function of settling time. The combination of 60 g/m<sup>3</sup> quicklime with 0.06–0.12 g/m<sup>3</sup> coagulation aid with low charge density led to the most efficient removal of Fe-tot and the lowest TSS values of the treated test water. However, all test batches exceeded the Fe-tot threshold value of 1.5 mg/L. By the initial supply of coagulant, the mass of settleable solids increased by a factor of 2 to 3, due to enhanced settling of both Fe oxy-hydroxides and calcium carbonate.

*Mesoscale process simulation.* The aim of this experiment was twofold: (i) combine the single treatment steps into a mesoscale process to demonstrate the applicability, and (ii) gain enough EHR substrate for dewatering tests and analysis. The experiment was conducted in a 1 m<sup>3</sup> reactor for two test waters according to a detailed treatment plan: (i) filling the reactor, (ii) aeration for 40 min by gas lance, concurrent supply of 60 g/m<sup>3</sup> of slaked quicklime, (iii) short-stirred dosing of 0.06 g/m<sup>3</sup> coagulation aid, (iv) water quality monitoring over a 4 h settling period, (v) separation of settled residue, (vi) dewatering tests and analysis of EHR constituents. While the TSS concentration fell below the threshold value within 4 h of settling time, the Fe-tot concentration came close but missed the threshold value of 1.5 mg/L (Fig. 3).

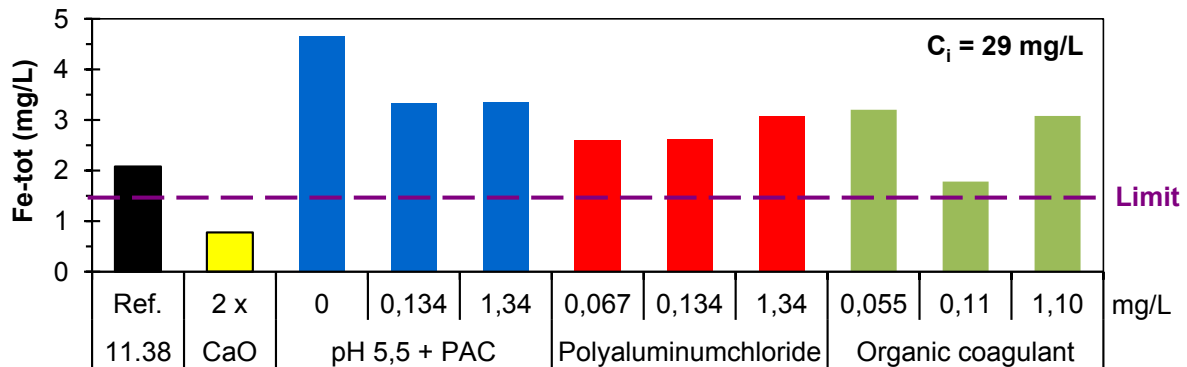
*Optimized iron precipitation.* To further improve the efficiency of Fe precipitation, additional approaches were tested in batch experiments with 1 L glass cylinders:

- Supply of varied doses of additional coagulants prior to the supply of slaked quicklime, including a highly cationic organic product and a weakly cationic polyaluminum chloride (PAC). For the latter, an adjusted pH ~5.5 was tested in addition to the primordial pH condition. Fe-tot concentrations after 2 h of settling time did not go below the threshold value (Fig. 4).

- Test of a novel dosing sequence by split supply of slaked quicklime, with a dose of 12 g/m<sup>3</sup> into the oxidation step, and a dose of 48 g/m<sup>3</sup> into the flocculation zone *after* the supply of coagulation aid. The aim was to co-precipitate colloidal Fe(III) through initiated precipitation of calcite. Fe-tot concentration fell below 1 mg/L, thus fulfilling the official threshold value of 1.5 mg/L (Fig. 4). However, the TSS concentration exceeded the 30 mg/L threshold value by 60 %, due to delayed settling of calcite particles. This shortcoming can be compensated by a turbidity dependent dose rate control.



**Figure 3** Concentration of total suspended solids (left) and total iron (right) of the two treated test waters as a function of settling time. Coagulation aid was intermixed within the first 3 min of time scale.



**Figure 4** Remnant Fe-tot concentration from initially 29 mg/L after 2 h of settling by testing varied final concentrations of coagulants (PAC = polyaluminum chloride and organic product) at primordial pH or adjusted to pH 5.5, as well as split supply of quicklime (CaO) relative to a reference batch with previous treatment.

**Scaling factor.** The aim was to determine a downscaling factor based on Fe-tot concentration between a running treatment plant (Schleinhain, combined effluent water) and a 1 L static batch experiment that mimicked the treatment process. Carried out on four sampling dates in October 2014, an average downscaling factor of  $3.0 \pm 1.1$  was obtained. Taking into account experimental and analytical uncertainties, this factor corresponded to an upscaling factor of 0.3–0.5 from bench scale results to full scale plant operation.

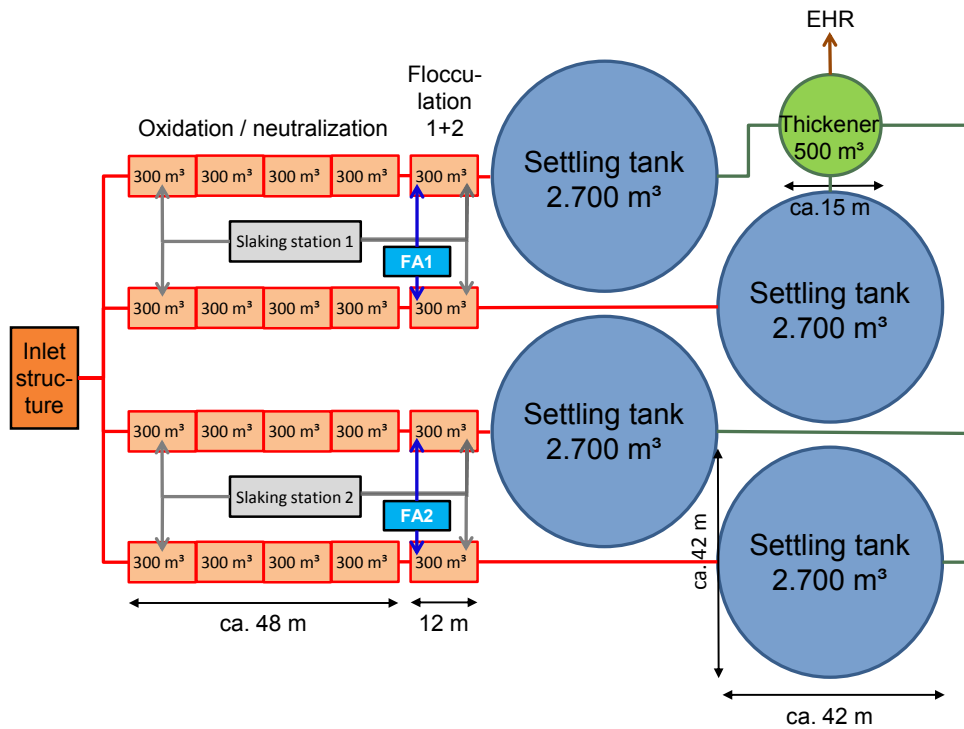
**Dewatering.** Applying the standardized capillary suction time (CST) method on the EHR residues collected from mesoscale process simulation, values of  $<3 \text{ kg s}/(\text{g dw})$  indicated good ability for dewatering (Bahrs et al. 1994). Gravitational thickening of these residues was simulated in a plexiglass cylinder by applying constant overpressure of  $+285 \pm 15 \text{ hPa}$ . Within 48 h,  $\sim 40 \%$  of initial volume got lost. To keep the residues suitable for pumping, solids content shall not exceed 10 M%. Hence, a yield of 200 to 360 m<sup>3</sup>/d of thickened residue would be expected for the anticipated full-scale throughput of 120 m<sup>3</sup>/min (Table 1). Extended dewatering was simulated by centrifugation at 4,400 g. While it would further increase the solids content and lower the load of EHR residue, filter pressing technology would

be very costly. Based on the solids content of naturally dehydrated EHR deposited in diked cells of the Schleehain mine, the size and loading capacity of prospective disposal areas within active dump sites were estimated for the planned treatment plant.

**Table 1** Process parameters obtained from mesoscale process simulation to size full-scale mass flow parameters. CST (capillary suction time) is a standardized method to quantify the ability for dewatering.

Experimental process step	Parameter, unit	Test water		Mass flow estimate for full-scale throughput of 120 m <sup>3</sup> /min	Test water	
		1	2		1	2
Sedimentation (4 h)	Solids content, g/kg	65	22	Settleable solids, L/m <sup>3</sup>	1,49	3,44
	CST, kg s (g dw) <sup>-1</sup>	0,62	2,24	Residue flow rate, m <sup>3</sup> /d	257	594
Gravitational thickening (5 d)	Loss of volume, %	41	50	Estimated loss of volume, %	40	40
	Solids content, g/kg	137	48	Thickened residue yield, m <sup>3</sup> /d	154	357
Dewatering simulated, 4400*g	Solids content, g/kg	380	193	Dewatered residue yield, m <sup>3</sup> /d	50	78
				Dewatered solids yield, t/d	21,8	16,4

*Gross design of treatment process.* Taking all results together, a four-routed treatment plant was sized for anticipated throughput of 120 m<sup>3</sup>/min. The engineered concept included one inlet structure, serial oxidation reactors, two-step flocculation reactors, four settling tanks, two quicklime slaking reactors, two make-up reactors for flocculation aid (FA), and one thickener (Fig. 5). A second thickener shall be considered for technical redundancy.



**Figure 5** Gross-sized process flow scheme of planned mine water treatment plant (see text).

### Results on Handling Treatment Residues

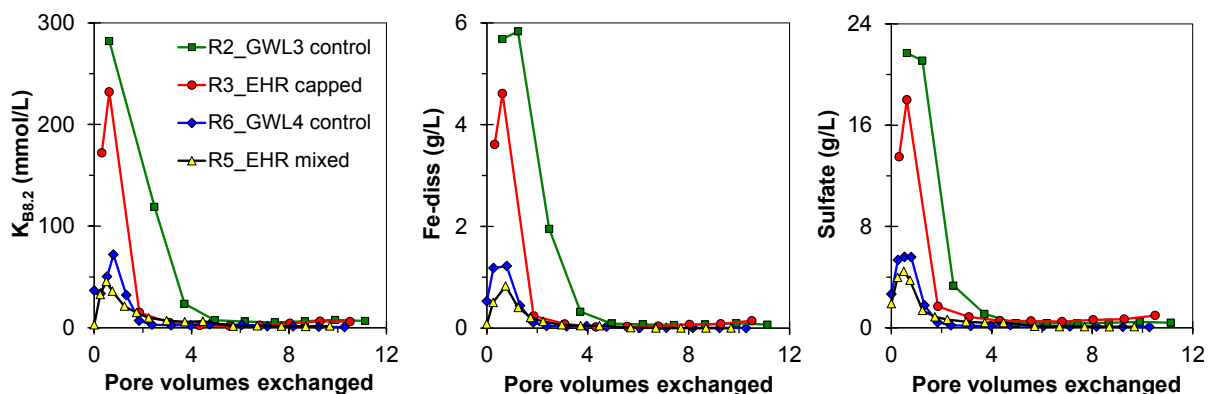
*Permissible utilization.* Precipitated residues are an undesired, but technically inevitable by-product of mine water treatment, to be handled as “waste” according to the EU conformable Closed Substance Cycle Waste Management Act. This means that re-use or recycling is to be favored over backfilling or dumping. Because the EHR contains acid buffering capacity (mainly Ca/Mg carbonates), and heavy metal and arsenic contents are expected to comply with the LAGA Z0 indicator values, non-risky

emplacement within mining dumps appears licensable. The mine operator was authorized the disposal of mine water residues within active dump sites of the operating Schleenhain lignite mine in 2009. Thickened EHR suspension is pumped from the treatment plant into diked cells later on buried by continued dumping of overburden (Jolas et al. 2013).

*Process simulation on effects and fate of buried EHR.* The main research question was whether EHR is safe to be embedded within excavated tertiary sands that liberate acidity due to pyrite oxidation. The processes of groundwater recharge and rise were simulated with columns containing settled residues sandwiched between excavated tertiary sands. Reactors devoid of residues served as a control. All test substrates and deep groundwater were collected from the field site and major properties characterized before and after running the experiments. Synthetic rain water was used to mimic recharge conditions. Figure 1 shows a sketch of the experimental setup.

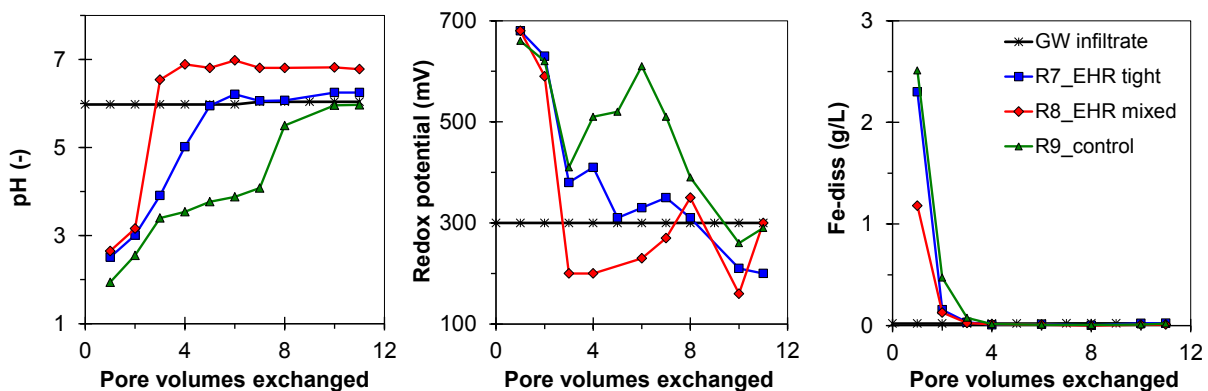
*Key properties of test substrates.* The overburden test substrates (medium sands) collected from two aquifers (GWL3 and GWL4) differed considerably with respect to intrinsic acidity. Acidity of GWL3-sand was almost ten times higher than that of GWL4-sand, consistent with a five times higher sulfide content. Of similar size were total porosity (0.45 and 0.40) and DARCY hydraulic conductivity ( $1.2 \cdot 10^{-5}$  and  $4.8 \cdot 10^{-5}$ ). The settled EHR collected from a dump cell had by 90 % particles  $< 2 \mu\text{m}$ , bulk dry density of  $0.15 \text{ g/cm}^3$ , total porosity of 0.95, DARCY  $K_f$  of  $2.5 \cdot 10^{-8}$ , and alkalinity of  $6.1 \text{ mol/kg dw}$ . Other properties are reported in Ulrich et al. (2015). Various pre-experiments were carried out to determine hydraulically active porosity, Van-Genuchten parameters, and acid-base reactivity in order to size the reactors and the load ratio of test substrates. The aim was to achieve breakthrough of acidity or alkalinity in the effluent within the experimental runtime. The resulting concept of load size and layer arrangement of the experimental reactors is described elsewhere (Jolas et al. 2013, Ulrich et al. 2015).

*Simulation of groundwater recharge.* This scenario was simulated by infiltrating synthetic rainwater from the uncovered top of four reactors (R). R3 contained a 7 cm thick layer of EHR on top of a 20 cm GWL3-sand layer. Despite a 3.2-fold surplus of alkalinity relative to the substrate's acidity in the reactor, breakthrough of alkalinity did not occur. However, the concentrations of acidity, dissolved iron and sulfate in the effluent were lower and declined more rapidly than in the reference reactor R2 devoid of EHR (Fig. 6). Detailed mass balance proved that this output was not only driven by hydraulic elution, but also by pyrite oxidation progressing in the tertiary sand substrate. Capping this substrate by EHR abated pyrite oxidation and the transport of acidity, dissolved iron and sulfate into deeper aquifers. Over the course of the experiment, only 16 % of the EHR alkalinity got consumed, probably due to shortcut flow through cracks that formed whilst progressive dewatering. Reactor R5 contained a 10 cm thick layer of EHR mixed with GWL4-sand overlain by 37 cm of pure GWL4-sand. Due to a 1.25-fold surplus of acidity in the reactor, breakthrough occurred after two pore volumes exchanged. Nevertheless, effluent acidity, dissolved iron and sulfate concentrations were lower and redox potential was higher than in the reference reactor R6 devoid of EHR (Fig. 6). The EHR alkalinity was fully consumed, showing that mixing of the substrates enhanced the chemical reactivity.



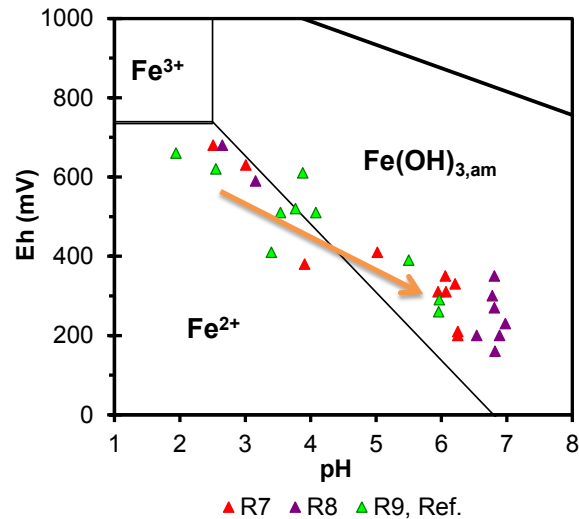
**Figure 6** Course of acidity, Fe-diss, and sulfate concentration as a function of pore volumes exchanged in reactor R2 (control w/ GWL3-sand), R3 (GWL3-sand w/ EHR on top), R5 (GWL4-sand on top of mixed EHR), and R6 (control w/ GWL4-sand) with simulated groundwater recharge.

*Simulation of groundwater rise.* This scenario was simulated by infiltrating original groundwater from bottom to top of three closed reactors. R7 and R8 contained EHR layers sandwiched between a GWL4-sand layer on top and a bottom GWL3-sand layer (50 cm thick in each reactor). While R7 carried a compact layer of EHR 12 cm thick, the same amount of EHR was mixed with GWL4-sand to a 23 cm thick layer in R8. Both reactors contained a 2-fold surplus of alkalinity relative to the substrate's acidity in the reactor. The reference R9 contained 50 cm of GWL4-sand on top of 50 cm of GWL3-sand. Within seven pore volumes exchanged, the effluent pH slightly increased from pH 2 to pH 4. Thereafter, the effluent pH converged to pH 6.0 of infiltrated groundwater (Fig. 7). The effluent of R7 reached the same pH value already with five pore volumes exchanged, and the effluent of R8 even exceeded this pH value after two pore volumes exchanged due to breakthrough of alkalinity. Correspondingly, the redox potential fell from 700 to 200 mV, eventually approaching the infiltrated groundwater value of 300 mV. The export of dissolved iron (Fig. 7), sulfate, and acidity (not shown) from reactors containing EHR was lower than from the reference reactor. Detailed mass balance showed that intrinsic alkalinity of EHR retained substantial amounts of the acidity stored, and generated over the course of the experiment. At least 15 % of the EHR alkalinity was consumed. About twice this proportion of EHR alkalinity was consumed in R8, containing the same amount of EHR but mixed with tertiary sand. This result demonstrates that mixing alkaline EHR with acid overburden substrate will increase its buffering efficacy.



**Figure 7** Course of pH, redox potential, and Fe-diss concentration as a function of pore volumes exchanged in reactor R7 (tight EHR layer), R8 (mixed EHR layer) and R9 (control) with simulated groundwater rise.

By depicting the experimental results in a stability field diagram of iron as a function of pH and redox potential (Fig. 8), one can see that upon initial elution of accumulated  $\text{Fe}^{2+}$ , the presence of EHR under simulated groundwater rise will quickly shift the environmental conditions towards the thermodynamically favored solid Fe hydroxide phase which is known as sparingly soluble. The results demonstrate that carbonate alkalinity in EHR acts as a buffer against acidity stored or generated by overburden substrates containing oxidizable sulfides. This prevents low pH conditions favoring acid dissolution of Fe hydroxides. In addition, redox potential did not fall below 200 mV, hence reductive EHR dissolution would not be expected. The low organic carbon contents of the test substrates (<0.1 M% in tertiary sand, 1.0 M% in EHR, and 3 mg/L DOC in groundwater) appear unfavorable for enhanced microbial Fe(III) reduction. Eventually, buried EHR would equilibrate with conditions typical for deep aquifers (pH ~6,  $E_H$  ~300 mV, low microbial activity). Nevertheless, more research focusing microbial effects on EHR and site-specific determination of biogeochemical process parameters is needed to predict the long-term fate and stability of EHR buried within tertiary overburden.



**Figure 8** Fe-O-H stability diagram (45 mM Fe-tot, 10 °C) depicting effluent data from three reactors with simulated groundwater rise; arrow indicates shifting within the experimental runtime.

## Conclusions

Process parameters determined from task-specific simulation experiments are decisive for many purposes of environmental engineering. This contribution exemplifies their value for different objectives, (i) design and gross-sizing of process technology for mine water treatment in order to meet official threshold values for discharge, and (ii) prediction of effects and fate of iron-rich treatment residues buried together with tertiary overburden substrates that liberate acidity upon groundwater recharge and rise. Concerning the first task, this work demonstrated that Fe precipitation from mine water could be enhanced by modifying the treatment sequence. Adding slaked quicklime as a coagulant after the supply of coagulation aid accelerated the agglomeration and settling of colloidal iron oxyhydroxide particles.

Concerning the second task, the simulation experiments showed that alkalinity loaded EHR from mine water treatment is suited for storage in deep mine dumps. Because alkaline EHR successfully neutralized acidity from tertiary overburden, acid dissolution of Fe oxyhydroxides did not occur. Reductive EHR dissolution requires low redox potential <200 mV, which was not observed in the simulation experiments due to low organic carbon contents and thus microbial activity. However, further research is needed to study long-term microbial effects on EHR stability at dumping sites with higher organic carbon content. Burial of alkaline EHR from mine water treatment in deep dumps of active lignite mines can be considered a remedy against acid loading to groundwater and surface waters, thereby saving prospective costs for water conditioning of remaining pit lakes.

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