

# A novel electrochemical process for the recovery and recycling of ferric chloride from precipitation sludge

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**Abstract:** During wastewater treatment and drinking water production, significant amounts of ferric sludge (comprising ferric oxy-hydroxides and  $\text{FePO}_4$ ) are generated that require disposal. This practice has a major impact on the overall treatment cost as a result of both chemical addition and the disposal of the generated chemical sludge. Iron sulfide ( $\text{FeS}$ ) precipitation via sulfide addition to ferric phosphate ( $\text{FePO}_4$ ) sludge has been proven as an effective process for phosphate recovery. In turn, iron and sulfide could potentially be recovered from the  $\text{FeS}$  sludge, and recycled back to the process. In this work, a novel process was investigated at lab scale for the recovery of soluble iron and sulfide from  $\text{FeS}$  sludge. Soluble iron is regenerated electrochemically at a graphite anode, while sulfide is recovered at the cathode of the same electrochemical cell. Up to  $60 \pm 18\%$  soluble Fe and  $46 \pm 11\%$  sulfide were recovered on graphite granules for up-stream reuse. Peak current densities of  $9.5 \pm 4.2 \text{ A m}^{-2}$  and minimum power requirements of  $2.4 \pm 0.5 \text{ kWh kg Fe}^{-1}$  were reached with real full strength  $\text{FeS}$  suspensions. Multiple consecutive runs of the electrochemical process were performed, leading to the successful demonstration of an integrated process, comprising  $\text{FeS}$  formation/separation and ferric/sulfide electrochemical regeneration.

**Key words:** electrochemical sulfur recovery; ferrous oxidation; iron recovery

## 1 Introduction

During conventional wastewater treatment, ferric salts (either as  $\text{Fe}_2(\text{SO}_4)_3$  or  $\text{FeCl}_3$ ) are typically dosed into primary influent (pre-precipitation), into the aerobic tank (co-precipitation) or into secondary effluent (post-precipitation), to achieve phosphorus precipitation and coagulation of organic solids. The precipitate thus obtained consists mostly of  $\text{FePO}_4$ , ferric (oxy)hydroxides and organic solids. This process entails significant costs associated mostly with the addition of the ferric salts and disposal of the chemical sludge thus generated. This ferric sludge can be used as a source of phosphorus and ferric iron. The latter, if recovered, can be re-utilized in the process, potentially creating significant savings for the water industry. The effectiveness of sulfide addition to ferric sludge (as phosphate or oxy-hydroxide) to achieve  $\text{FeS}$  precipitation and phosphorus recovery has been already proven (Ripl et al. 1988, Kato et al. 2006, Mejia Likosova et al. 2013b). In such a method, the addition of sulfide to the ferric sludge reduces ferric iron ( $\text{Fe(III)}$ ) to ferrous iron ( $\text{Fe(II)}$ ) leading to the precipitation of  $\text{FeS}$  particles, thus separating iron from any phosphate and opening to a potential route for iron recovery. After the recovery of phosphorus, iron and sulfur can potentially be separated and recycled within the process, i.e. iron can be recycled as  $\text{Fe(II/III)}$  to the phosphate precipitation and coagulation process while sulfide can be reused to generate more  $\text{FeS}$  from ferric sludge.

Sulfide is an electrochemically active compound and the anodic oxidation of aqueous sulfide has been studied and demonstrated by different authors (Lalvani and Shami 1986, Kelsall et al. 1999, Ateya et al. 2003, Ateya et al. 2005, Dutta et al. 2008, Dutta et al. 2010, Pikaar et al. 2011). The range of oxidation products is affected by anode materials and imposed potentials (Kelsall et al. 1999), and include elemental sulfur ( $\text{S}^0$ ), polysulfide ( $\text{S}_n^{2-}$ ), sulfate ( $\text{SO}_4^{2-}$ ), sulfite ( $\text{SO}_3^{2-}$ ) and thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ).

Efficient removal of sulfide from dilute aqueous solutions at circum-neutral pH via oxidation to  $\text{S}^0$  has been demonstrated on graphite anodes (Dutta et al. 2008), whereby elemental sulfur was deposited onto the anode surface. Sulfur was effectively removed because it adsorbed onto the anode surface. Dutta and co-workers demonstrated a method for in-situ recovery of the electrodeposited  $\text{S}^0$  on the electrode. This method consists of switching the polarity of the electrodes, i.e. periodic switching between anodic sulfide oxidation to  $\text{S}^0$  and cathodic sulfur reduction to sulfide. During cathodic operation, the previously deposited  $\text{S}^0$  is reduced

to sulfide. As a result, a concentrated sulfide solution can be recovered from the same electrochemical cell used for the sulfide oxidation to sulfur. However, a big fraction of the elemental sulfur was reduced to polysulfides when batch experiments were performed without pH control, during which the pH varied between 7.3-11.4 (Dutta et al. 2008).

In a previous study, we found that freshly generated  $\text{FeS}_x$  particles are reactive towards anodic oxidation to elemental sulfur on graphite electrodes (Mejia Likosova et al. 2013a).

In this work, we demonstrate the feasibility of an electrochemical process for the resource-efficient recovery of soluble iron and sulfide from FeS sludge. The process is based on the electrochemical oxidation of sulfide (in the form of particulate FeS) to  $\text{S}^0$  (reaction 1), and partially sulfate (reaction 2) (Mejia Likosova et al. 2013a), with consequent release of soluble ferrous ions in solution. Soluble  $\text{Fe}^{2+}$  is then oxidised to ferric hydroxide, and subsequently to free ferric ions (reaction 4) as the pH drops to < 3 due to the acidity generated by the ferric hydroxide (reaction 3) and sulfate (reaction 2) formation. As the formed  $\text{S}^0$  is bound to the anode surface, it can be subsequently reduced back to sulfide upon polarity switching of the electrode, the only net input being electricity. In the system described above, the reactions occurring at the anode and their redox potentials vs. SHE are listed in Table 1.

**Table 1.** Anode and Cathode reactions and their redox potential.

<b>Oxidation Reaction (Anode)</b>	<b>Redox Potential [V]</b>
(1) $\text{FeS} \rightarrow \text{Fe}^{2+} + \text{S}^0 + 2\text{e}^-$	+0.06 <sup>I</sup>
(2) $\text{FeS}_{(s)} + 4\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^-$	-0.09 <sup>II</sup>
(3) $\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 3\text{H}^+ + \text{e}^-$ (at pH>3)	0.51 <sup>III</sup> (at pH 3.0)
(4) $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ (at pH<3)	+0.771 <sup>IV</sup>
<b>Reduction Reaction (Cathode)</b>	<b>Redox Potential [V]</b>
(5) $\text{S}^0 + 2\text{e}^- \rightarrow \text{S}^{2-}$	-0.476 <sup>I</sup>

<sup>I</sup> Standard redox potential calculated based on a FeS solubility constant of  $K_{sp}=8 \times 10^{-19}$  (Perry and Green 2008) and a standard redox potential of -0.476V for the reaction  $\text{S}^0 + 2\text{e}^- \rightarrow \text{S}^{2-}$  (Dutta et al. 2008).

<sup>II</sup> Standard redox potential calculated based on a standard redox potential of  $E^0=-0.22\text{V}$  for the reaction  $\text{S}^{2-} + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^-$  (Drake et al. 2006).

<sup>III</sup> Redox potential at pH 3 calculated with the Nernst equation after calculating a standard redox potential

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(pH 0) of  $E^\circ = -0.612$  V based on a  $\text{Fe}(\text{OH})_3$  solubility constant of  $K_s = 4 \times 10^{-38}$  at  $25^\circ\text{C}$  and a water self-ionization constant of  $K_w = 1 \times 10^{-14}$  at  $25^\circ\text{C}$  (Perry and Green 2008).

<sup>IV</sup> (Bard and Faulkner 2001).

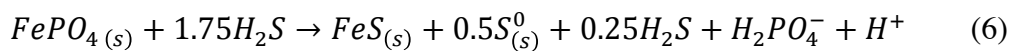
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In this study, the recovery of soluble iron and sulfide according to the proposed process has been demonstrated. Additionally, the feasibility of the full phosphorus and ferric recovery process with real sludge was established. For this work, carbon-based electrode materials were chosen, based on their proven reactivity with FeS, low cost and wide availability.

## 2 Materials and methods

### 2.1 Preparation of synthetic FeS precipitate and dilute synthetic, dilute real and full-strength real FeS suspensions for electrochemical anodic oxidation experiments

Synthetic FeS precipitate was prepared by reaction of synthetic 0.1 M ferric phosphate ( $\text{FePO}_4 \cdot 4\text{H}_2\text{O}$ , 24% Fe) with continuing dosing of a 0.8 M sodium sulfide solution ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , reagent grade), up to 1.75 S:Fe molar ratio at pH 4 (these conditions were found to be optimal for FeS formation and separation) within 30 minutes as described elsewhere (Mejia Likosova et al. 2013b). The pH was controlled using a 3 M HCl solution. The reaction of ferric phosphate and sulfide, at a S:Fe molar ratio of 1.75 and slightly acidic conditions, can be represented by the following stoichiometry (Kato et al. 2006, Firer et al. 2008):



The resulting synthetic precipitate is a combination of nanoparticulate mackinawite (FeS) and elemental sulfur ( $\text{S}^0$ ) (Mejia Likosova et al. 2013a). The suspension was divided into two 50-mL Falcon tubes without leaving any air headspace and centrifuged at 2,100 g for 5 minutes to enhance separation of the gravity-settled FeS particles. The supernatant with residual soluble sulfide and phosphate in solution was removed. A dilute synthetic FeS suspension ( $103 \pm 46$  mg Fe  $\text{L}^{-1}$ ) was prepared using 4.2 mL of the settled FeS particles diluted up to 300 mL in a 0.03 M NaCl solution. The salt addition was provided to sustain the selective migration of  $\text{Na}^+$  ions to the cathode throughout the reaction in order to guarantee the electroneutrality of both

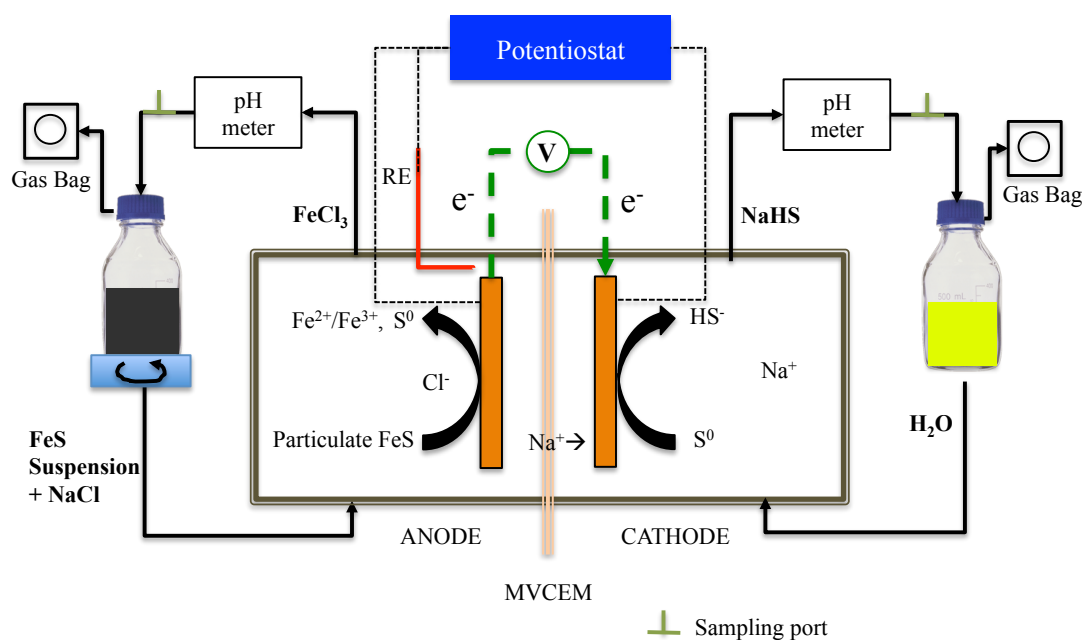
anodic and cathodic compartments, in addition to keeping the internal resistance as low as possible (see section 2.2).

Following the same process described above, real chemical ferric sludge (with following concentrations: total iron  $9.4 \pm 0.8$  g Fe L<sup>-1</sup>, chemical oxygen demand (COD)  $17 \pm 3$  g COD L<sup>-1</sup>, total suspended solids (TSS)  $57 \pm 8$  g TSS L<sup>-1</sup> and volatile suspended solids (VSS)  $18 \pm 2$  g VSS L<sup>-1</sup>) from a local full-scale drinking water treatment plant (DWTP) was used to precipitate real FeS sludge. After sulfide addition as described above, the resulting sludge was divided into three 50-mL Falcon tubes without leaving any air headspace and centrifuged at 2,100 g for 15 minutes to enhance sedimentation of the FeS particulates. A dilute real FeS suspension ( $84 \pm 11$  mg Fe L<sup>-1</sup>) was prepared similarly as described above for the dilute synthetic FeS suspension. A full-strength real FeS suspension ( $3.0 \pm 0.2$  g Fe L<sup>-1</sup>) was prepared using the settled FeS sludge from the three Falcon tubes (~30 mL in total) and diluted using 300 mL of a 0.15 M NaCl solution.

## 2.2 *Two-compartment electrochemical reactor design and operation*

The two-compartment electrochemical cell consisted of 2 parallel Perspex frames (internal dimensions of 20x5x2 cm) separated by a monovalent cation exchange membrane (MVCEM, CMS Monovalent Selective, Ameridia, USA). Three sets of experiments were performed using three different carbon-base electrodes: graphite granules (El Carb 100, Graphite Sales Inc., USA), graphite plates (Morgan AM&T, Sydney) and Reticulated Vitreous Carbon (RVC, Duocel RVC Foam, ERG Materials and Aerospace Corporation, USA). In the first set of experiments, both compartments were filled with graphite granules as working and counter electrodes (WE, CE). The graphite granules have diameters of 1.5-6 mm and a porosity of 45%, leading to a mean nominal surface area of 1,000 cm<sup>2</sup> in each compartment (Freguia et al. 2008). Before using the graphite granules, a pre-treatment with acid and base to remove impurities was performed as explained elsewhere (Dutta et al. 2008). Graphite plates (100 cm<sup>2</sup> in projected surface area) were embedded in the graphite granules and used as current collectors in both anode and cathode. In the second set of experiments, only graphite plates were used as working and counter electrodes, reducing the nominal contact area to 100 cm<sup>2</sup> each. Finally, in the third set of experiments, 2 rectangular pieces of reticulated vitreous carbon (RVC) foam (pore size 20 PPI, 3% density) with

dimensions 20x5x2 cm each (nominal surface area 2,200 cm<sup>2</sup>) were used as working and counter electrodes. Figure 1 gives a schematic diagram of the 2-compartment electrochemical cell.



**Fig. 1.** Schematic diagram of the 2-compartment electrochemical cell. FeS suspension is recirculated through the anode compartment, where oxidation of FeS particles to S<sup>0</sup> and soluble iron occurs. Likewise, S<sup>0</sup> is reduced to S<sup>2-</sup> at the cathode after reversing the polarities of the electrodes.

FeS suspension was recirculated at 6 L h<sup>-1</sup> around the anode compartment, where reactions 1-4 occurred. The total anode liquid volume (inclusive of an external bottle in the recirculation loop) was 300 mL. The FeS suspension was continuously stirred by means of a magnetic stirrer in order to avoid settling of the FeS particles and to guarantee a homogeneous feed to the anode. Previously deposited elemental sulfur is reduced to sulfide at the cathode. The catholyte was initially water only and it was recirculated around the cathode compartment. Sulfide formation and Na<sup>+</sup> migration from the anode increased the catholyte salinity as the reaction proceeded. The recirculation was set to 6 L h<sup>-1</sup> using a multi-channel peristaltic pump.

At the anode, simultaneous oxidation of FeS to sulfate and Fe<sup>2+</sup> to Fe(OH)<sub>3</sub> (equations 2 and 3) drove the pH down until iron became soluble (pH < 3) (Mejia Likosova et al. 2013a). Conversely, at the cathode, sulfide generation increased the solution pH to >10. At the anode, FeCl<sub>3</sub> was recovered in soluble form due to the acidic conditions created. Na<sup>+</sup> cations migrated through the MVCEM to the cathode forming a solution of NaHS. Two pH probes (Ionode Pty Ltd., Australia) were placed in the anodic and

cathodic recirculation lines to measure the pH of both compartments. A glass body Hg/Hg<sub>2</sub>Cl<sub>2</sub> Calomel reference electrode, KCl 3.5 M, (Select Scientific, E<sup>0</sup> = +0.250 mV vs. SHE) was placed near the anode. Anode and cathode were connected through a potentiostat (VSP Modular 5 channels potentiostat, BioLogic Science Instrument, France) and the anode half-cell potential was controlled to either +0.8 V vs. SHE or +1.3V vs. SHE.

Batch experiments were run sequentially 3-4 times, each time reversing the cell polarity to enable dissolution of the elemental sulfur precipitated in the previous run. Three hundred mL of the FeS suspension (see section 2.1) were used to fill the anodic compartment. Reverse Osmosis (RO) water was used to fill the cathodic compartment (300 mL inclusive of an external bottle in the recirculation loop). Before starting with the batch runs, one of the two electrodes (anode) was pre-loaded with elemental sulfur (S<sup>0</sup>) via electrochemical oxidation of ferrous sulfide, with the cathode operating as hydrogen-producing counter electrode (this was named Run 0). Anaerobic conditions were achieved by sparging both compartments and solutions with nitrogen. Two gas bags filled with nitrogen were connected to the recirculation loops of anode and cathode, to avoid the intrusion of oxygen into the system by applying a positive pressure of nitrogen. Each run lasted for 1 to 70 h depending on the electrode (see section 3.1) and sludge strength. The anode potential, as well as the current were recorded using the EC-Lab software for the VSP BioLogic potentiostat (see section 2.3). Liquid samples from both anode and cathode were collected throughout the experiment for the measurement of iron species and various sulfur compounds, respectively (methods detailed in section 2.4).

### *2.3 Potentiostatic measurements and calculations*

Potentiostatic measurements and control were performed using a VSP Modular 5 channels potentiostat (BioLogic Science Instrument, France). Current and voltage data were recorded every 60 s using the EC-Lab® software. Current density was defined as the average current in ampere per square metre of projected electrode surface area (0.01 m<sup>2</sup> in all experiments, equivalent to the membrane size).

## 2.4 Chemical analyses

Ion Chromatography (IC, Dionex 2010i) was used to measure the different anionic sulfur species, i.e. sulfide, sulfate, sulfite and thiosulfate, from anode and cathode according to the method developed by Keller-Lehmann et al. (2006). Samples were preserved in previously prepared Sulfide Anti-Oxidant Buffer (SAOB) solution prior to IC analysis. SAOB solution was prepared following the guidelines explained elsewhere (Keller-Lehmann et al. 2006, Dutta et al. 2008). Total iron and sulfur in the anode and cathode samples were determined using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES, Perkin Elmer Optima 3300DV) as explained elsewhere (Mejia Likosova et al. 2013b). The determination of total iron was possible after acidic digestion of the sample (5% and 10% nitric acid when feeding synthetic FeS and real FeS suspension to the anode, respectively). Before acidic digestion, oxidation of the sulfide present in the samples to sulfate ( $\text{SO}_4^{2-}$ ) was performed under alkaline conditions ( $\text{pH}>12$ ) with excess peroxide (Cadena and Peters 1988), in order to avoid any loss of S in the form of  $\text{H}_2\text{S}$  during the acidic digestion (Mejia Likosova et al. 2013b).

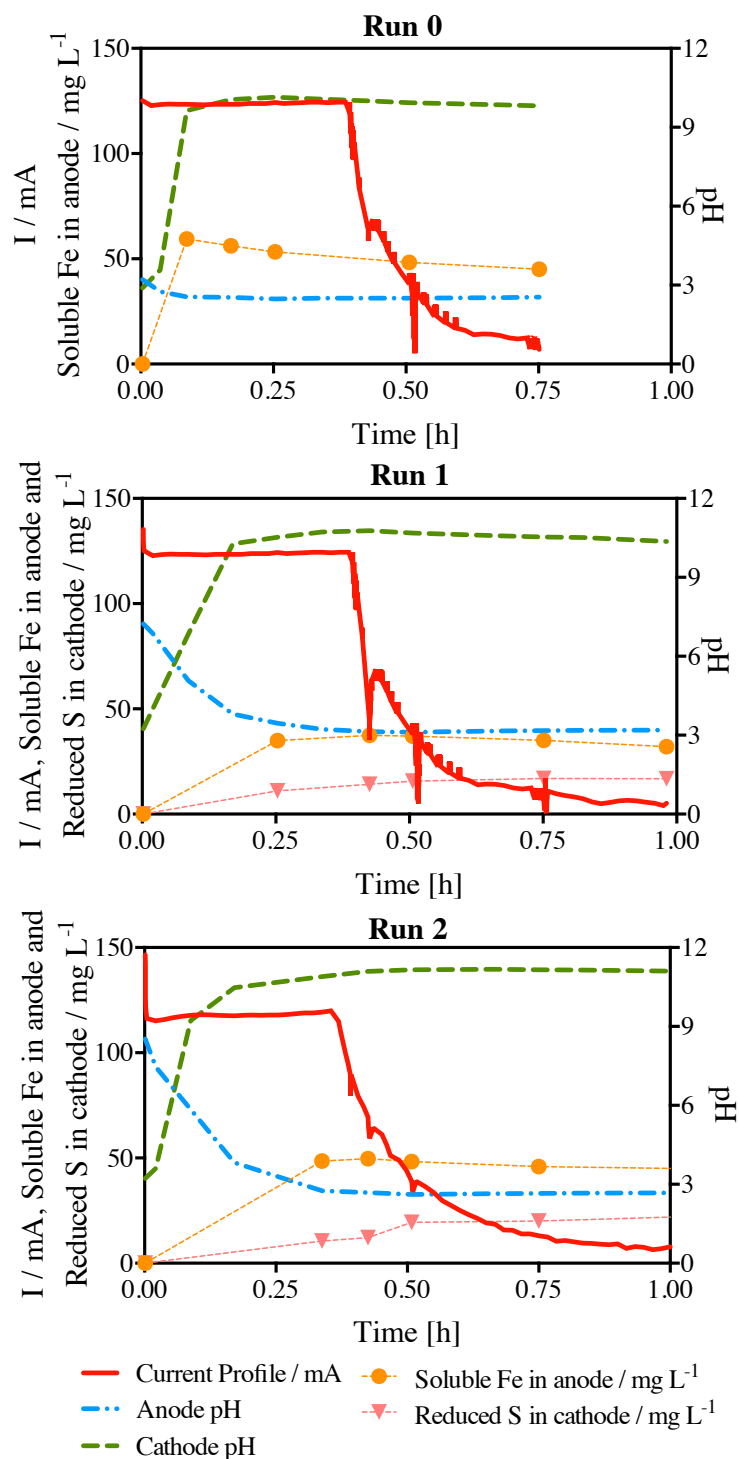
## 3 Results and Discussion

### 3.1 Soluble iron and sulfide recovery from dilute synthetic, dilute real and full strength real FeS suspensions on graphite granules at different anode potentials

In order to prove the concept of the proposed iron and sulfide recovery electrochemical process, 3-4 consecutive runs for each FeS suspension were performed as described above. Figure 2 shows the current profile, anode and cathode pH profiles, soluble iron profile in the anodic solution and reduced sulfur (as sulfide + polysulfide) profile in the cathodic solution during the 3 consecutive runs of the process fed with dilute synthetic suspension at +0.8V vs. SHE anode potential. In all runs, the anode pH dropped from an initial value of  $6.3\pm 2.8$  to a final pH of  $2.8\pm 0.3$  as a consequence of the oxidations of soluble ferrous to ferric hydroxide and sulfide to sulfate, according to equations 1-4. The cathode pH increased from an initial value of  $3.1\pm 0.2$  to a final pH of  $10.1\pm 0.9$  as a consequence of the reduction of elemental sulfur to sulfide and polysulfide, according to equation 5. A similar peak current density of  $13.3\pm 6.3 \text{ A m}^{-2}$  was reached in all experiments. Despite the continuous

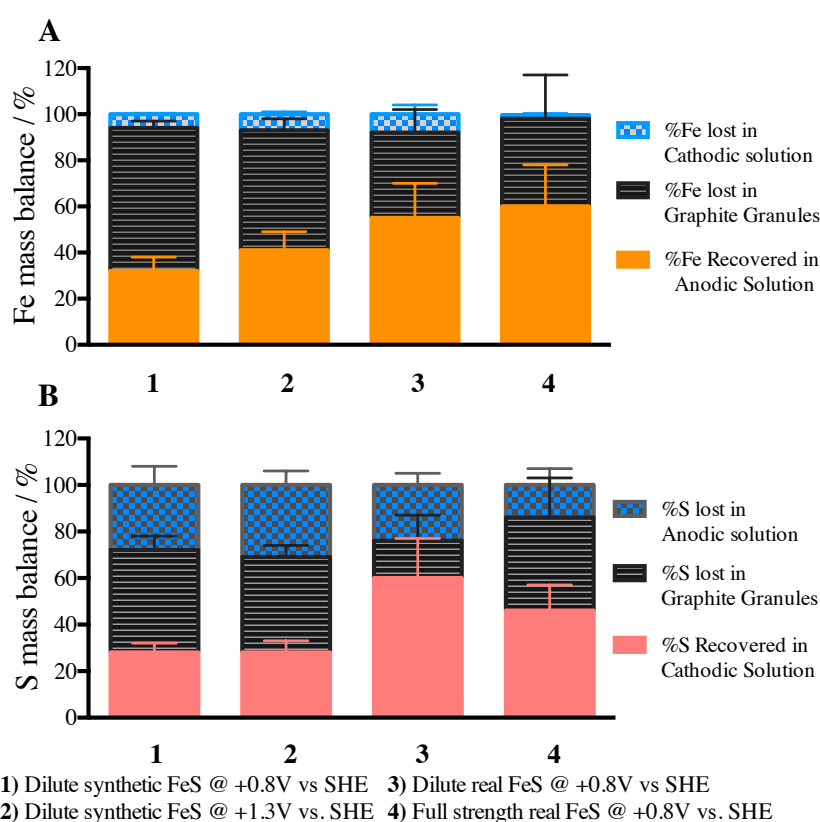


current flow during the first 30 minutes of experiment, the soluble Fe and reduced S (as sulfide and polysulfide) concentrations did not seem to increase after 15 minutes.



**Fig. 2.** Current profile [mA], anode and cathode pH profiles, soluble iron profile in the anodic solution [ $\text{mg Fe L}^{-1}$ ] and reduced sulfur (as sulfide + polysulfide) profile in the cathodic solution [ $\text{mg S L}^{-1}$ ] during 3 consecutive runs of the proposed electrochemical process controlled at  $+0.8\text{V}$  vs. SHE anode potential for a dilute synthetic FeS suspension ( $123 \pm 16 \text{ mg Fe L}^{-1}$ ). Short, negative spikes in current profiles are caused by minor disturbances due to liquid sampling events.

In Figure 3A and B, the overall Fe and S balances of the process are shown, respectively. In all the experiments, soluble iron was recovered in the anodic solution (Figure 3A). Sulfide never appeared in the anodic solution at the end of each run. However, up to  $28\pm 8\%$  and  $31\pm 6\%$  S was lost as sulfate in the anodic solution at  $+0.8\text{V}$  and  $+1.3\text{ V}$  vs. SHE, respectively (Figure 3B). The cathode side generated reduced sulfur (as sulfide and polysulfide) from previously deposited elemental sulfur, with reduced sulfide recovery up to  $28\pm 5\%$ ,  $60\pm 17\%$  and  $46\pm 11\%$  when feeding dilute synthetic, dilute real and full strength real FeS suspensions, respectively.



**Fig. 3.** Fe and S mass balance of the proposed electrochemical process for dilute synthetic FeS suspension at  $+0.8\text{ V}$  and  $+1.3\text{ V}$  vs. SHE; and dilute real and full strength real FeS suspensions at  $+0.8\text{ V}$  vs. SHE. **A)** Fe recoveries measured as soluble Fe in the anodic solution at the end of each run. **B)** Reduced sulfur recovery measured as the sum of sulfide and polysulfide in the cathodic solution at the end of each run.

The graphite granules appear to consistently bind 40-70% of the incoming FeS, explaining the low recoveries of Fe and S. This was confirmed by the presence of FeS particles in the anode backwash and embedded within the graphite granules, as observed after opening the reactor. Although the unrecovered Fe and S seem to be

trapped as unreacted FeS in the reactor, further consecutive runs will need to be performed in order to fully understand the fate of the Fe and S during long-term cyclic operation. The results of the experiments from dilute synthetic, dilute real and full strength real FeS suspension feed at +0.8 V and +1.3 V vs. SHE are detailed in Table 2. Due to the higher FeS concentrations, the average run time increased from  $1.6\pm 0.2$  h to  $24\pm 6$  h when moving from dilute to full strength real FeS suspensions. However, Fe recoveries were statistically the same for the two strengths. The average power requirement when feeding full strength FeS suspensions was  $2.4\pm 0.5$  kWh kg Fe<sup>-1</sup>, which is only around half of that required for the dilute synthetic or real sludges ( $4.8\pm 3.2$  or  $4.4\pm 0.3$  kWh kg Fe<sup>-1</sup>, respectively). This can be attributed to the reduced Ohmic resistance in the system with the undiluted sludge, which is a result of the higher ionic conductivity of the latter ( $3.7\pm 0.2$  S m<sup>-1</sup> versus  $2.6\pm 0.1$  S m<sup>-1</sup>) after dilution with the NaCl solution.

<b>Table 2.</b> Summary of results for electrochemical recovery of Fe and S from FeS suspensions on graphite granules, graphite plates and reticulated vitreous carbon (RVC).							
<b>Suspension fed to anode with graphite granules as WE and CE</b>					<b>Electrode tested with dilute FeS</b>		
<b>Type of FeS suspension / Electrode</b>	<b>Dilute synthetic</b>	<b>Dilute synthetic</b>	<b>Dilute real</b>	<b>Full strength real</b>	<b>Graphite Plates</b>	<b>RVC</b>	<b>RVC</b>
<b>n</b>	10	4	4	4	3	1	3
<b>E anode (V vs. SHE)</b>	+0.8	+1.3	+0.8	+0.8	+0.8	+0.8	+1.3
<b>Fe fed to anode/ mg L<sup>-1</sup></b>	123±16	103±46	84±11	3000±200	96±9	102	102±33
<b>S/Fe molar ratio in Anode feed</b>	1.3±0.1	1.3±0.2	1.6±0.2	1.3±0.2	1.0±0.2	1.1	1.1±0.1
<b>Run time / h<sup>(i)</sup></b>	1.1±0.2	1.4±0.4	0.9±0.2	24±6	72±2	113	5.1±0.5
<b>Peak Current density/ A m<sup>-2(ii)</sup></b>	13.3±6.3	14.9±3.5	10.0±2.6	9.5±4.2	0.4±0.2	0.1	1.0±0.3
<b>Power requirement / kWh kgFe<sup>-1</sup></b>	4.8±3.2	8.2±1.7	4.4±0.3	2.4±0.5	9.1±4.6	2.2	21.5±6.5

<b>Ionic conductivity / S m<sup>-1</sup></b>	2.9±0.7	2.9±0.7	2.6±0.1	3.7±0.2	2.9±0.7	2.9±0.7	2.9±0.7
<b>Final anode pH</b>	2.8±0.3	2.6±0.5	2.3±0.2	2.1±0.2	4.7±2.0	4.69	3.2±0.4
<b>Final cathode pH</b>	10.1±0.9	10.6±0.1	8.3±3.5	11.9±0.4	8.1±2.5	6.13	10.1±1.0
<b>Soluble Fe recovered in anodic solution / %</b>	32±6	41±8	55±15	60±18	19±2	-	53±5
<b>Reduced S (as S<sup>2-</sup> and Polysulfide) recovered in cathodic solution / %</b>	28 ± 4	28 ± 5	60 ± 17	46 ± 11	15±3	-	20±5

<sup>1</sup>Each run was stopped once the anode reached a stable pH below 3 and/or the current approached zero asymptotically.

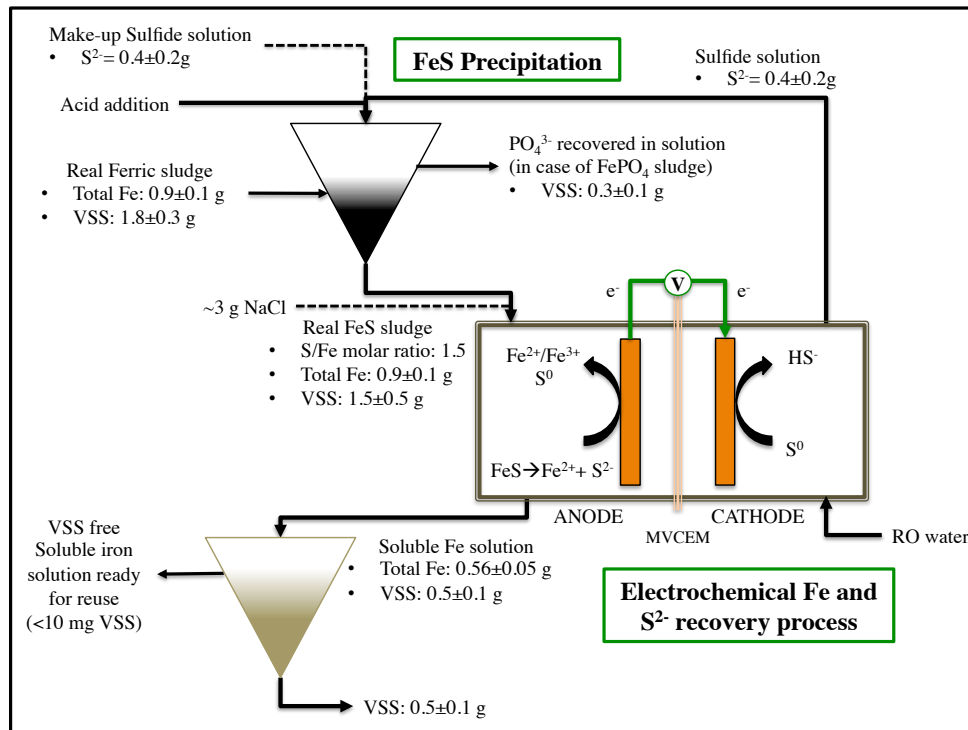
<sup>11</sup>Peak current density calculated as peak current (A) per projected electrode surface area (0.01 m<sup>2</sup>).

### 3.2 Soluble iron and sulfide recovery from dilute synthetic suspensions on different carbon based electrodes

Two other carbon based electrodes, namely graphite plates and reticulated vitreous carbon (RVC), were tested with dilute synthetic FeS suspensions. Low current densities and sulfide recoveries were achieved with both electrodes. The fast passivation of the graphite plates as a result of their low surface area led to a recovery of only 19±2% soluble iron when controlling the anode potential at +0.8 V vs. SHE. A slightly higher current density was achieved with the RVC at +1.3 V vs. SHE. However, the sulfide loss to sulfate was significant (only 20±5% S recovery as sulfide/polysulfide). Sulfate formation lowered the pH, thus rapidly solubilising all FeS, which increased iron recovery up to 53±5%. Considerably lower current densities were reached with the RVC at +0.8 V vs. SHE, suggesting that RVC may not be sufficiently reactive for FeS particle oxidation, despite its larger nominal surface area. The results of the experiments from dilute synthetic FeS feed at +0.8 V vs. SHE with graphite plates and RVC, and +1.3 V vs. SHE with RVC are detailed in Table 2.

### 3.3 FeS precipitation and electrochemical iron and sulfide recovery integrated process

In order to demonstrate the feasibility of an integrated FeS precipitation and electrochemical iron and sulfide recovery process with real sludge, 2 consecutive runs of the integrated process were performed. For this purpose, real FeS precipitate was fed to the anode of the 2-compartment electrochemical cell and the resulting cathode effluent was used to precipitate FeS from real ferric sludge. Black FeS particles were immediately formed when adding the cathode effluent to the real ferric sludge, confirming the feasibility of precipitating FeS particles using the cathode effluent. Comparable peak current densities ( $\sim 10 \pm 2 \text{ A m}^{-2}$  compared to  $9.5 \pm 4.2 \text{ A m}^{-2}$  when feeding full strength real FeS sludge precipitated with synthetic sulfide solution) were reached in the electrochemical process when feeding the real FeS suspension obtained from the reaction of the cathode effluent with the real ferric sludge. In Figure 4, a schematic representation of the integrated process and the total Fe, sulfide and the organic solids (measured as volatile suspended solids, VSS) mass balances are presented.



**Fig. 4.** Proposed integrated FeS precipitation and electrochemical iron and sulfide recovery process. The VSS, total Fe and S mass balances were performed after performing 2 consecutive runs of the integrated process, using the sulfide rich cathode effluent to precipitate FeS from real ferric sludge and feeding it to the anode of the 2-compartment electrochemical cell.

In the FeS precipitation process, around 83% organic solids co-precipitated with the FeS particles. Thus, VSS removal in the FeS precipitation process would be hardly feasible. After feeding the FeS-VSS suspension to the anode of the electrochemical cell, up to  $35\pm 12\%$  of the VSS exit with the anodic effluent. The remaining 65% of the VSS were retained in the graphite granular bed.

However, an increase in the VSS in the anode effluent was seen in the consecutive runs (i.e. 28%, 29%, 49% of the influent VSS were recovered in the effluent of run 0, 1 and 2 respectively), indicating that the VSS accumulation rate in the reactor may decrease cycle after cycle. Moreover, the VSS easily precipitate in the anode effluent as a result of the acidic conditions, leaving a VSS-free soluble iron supernatant. This was confirmed by measuring the VSS content in the supernatant (less than 10 mg VSS) after 15 min of settling in a 50 mL Falcon tube. Therefore, the best point for VSS removal would be in a clarifier fed with the anode effluent.

As shown in Figure 4, a make-up sulfide solution to the FeS precipitation process would be required in order to reach the stoichiometric S:Fe molar ratio of 1.5, as a result of the incomplete sulfide recovery in the cathode effluent ( $46\pm 11\%$  reduced S). Additionally, acid addition to the FeS precipitation process (down to pH 4) was required in order to achieve the separation of the FeS particles by gravity settling.

This study is a proof of concept and a stepping-stone towards the implementation of the integrated process at full scale. However, there are still some significant issues that will need to be addressed in the further development of the process. For instance, the recovered  $\text{FeCl}_3$  solution contains high NaCl concentrations, which could be problematic for reuse as a coagulant in a water treatment process. The objective of this study was to prove a process concept, hence NaCl was overdosed well above the stoichiometric requirement. In engineering applications, the NaCl addition should be lower to be as close as possible to the stoichiometric minimum, which would then provide a similar Fe to Cl ratio as in the original ferric chloride solution. Further work is required to fully understand the fate of the VSS entering the electrochemical recovery process. As explained in this study, most of the VSS appears to be captured in the granular graphite bed. This is a serious problem that may lead to fouling of the electrode over extended operating periods. However, an increase in the VSS fraction exiting in the anode effluent was seen after the first two runs, suggesting that the

recovery may be increasing further (and hence the accumulation be reduced) with consecutive runs. Still, additional experiments and longer operation of the process will need to be performed in order to better understand and address the fate of VSS during ongoing cyclic operation.

#### **4 Conclusions**

The aim of this research was to demonstrate the recovery of soluble iron and sulfide from FeS sludge via the proposed electrochemical process using carbon-based electrodes. Furthermore, to prove the feasibility of an integrated process for ferric chloride regeneration from wastewater or drinking water precipitation sludge, whereby the integrated process comprises FeS generation and electrochemical iron and sulfide recovery. After testing different concentrations of synthetic and real FeS suspensions at different anode potentials and carbon electrode materials, it was concluded that:

- Soluble iron and sulfide/polysulfide were partially recovered in the anodic solution and cathodic solution, respectively, at the applied anode potential of +0.8 V vs. SHE on graphite granules.
- Higher Fe recoveries were reached when feeding the process with real FeS suspension (~ 60% Fe recovery) compared to synthetic FeS suspension (up to 41% Fe recovery) on graphite granules.
- A large electrode surface area is beneficial for the process, however the RVC electrode material seems to have a poor electrochemical reactivity for the FeS particles, making this electrode unsuitable for the proposed iron and sulfide recovery process.
- The successful operation of the integrated FeS precipitation and electrochemical iron and sulfide recovery process was demonstrated. However, the addition of a make-up sulfide solution and an acid stream to the FeS precipitation process is still required in order to guarantee completion of the FeS formation reaction and precipitation of the formed particles.

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