



# Electrochemical sulfide removal and caustic recovery from spent caustic streams



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## ABSTRACT

Spent caustic streams (SCS) are produced during alkaline scrubbing of sulfide containing sour gases. Conventional methods mainly involve considerable chemical dosing or energy expenditures entailing high cost but limited benefits. Here we propose an electrochemical treatment approach involving anodic sulfide oxidation preferentially to sulfur coupled to cathodic caustic recovery using a two-compartment electrochemical system. Batch experiments showed sulfide removal efficiencies of  $84 \pm 4\%$  with concomitant  $57 \pm 4\%$  efficient caustic production in the catholyte at a final concentration of  $6.4 \pm 0.1$  wt% NaOH (1.6 M) at an applied current density of  $100 \text{ A m}^{-2}$ . Subsequent long-term continuous experiments showed that stable cell voltages (i.e.  $2.7 \pm 0.1$  V) as well as constant sulfide removal efficiencies of  $67 \pm 5\%$  at a loading rate of  $47 \text{ g}_{(\text{S})} \text{ L}^{-1} \text{ h}^{-1}$  were achieved over a period of 77 days. Caustic was produced at industrially relevant strengths for scrubbing (i.e.  $5.1 \pm 0.9$  wt% NaOH) at current efficiencies of  $96 \pm 2\%$ . Current density between 0 and  $200 \text{ A m}^{-2}$  and sulfide loading rates of  $50\text{--}200 \text{ g}_{(\text{S})} \text{ L}^{-1} \text{ d}^{-1}$  were tested. The higher the current density the more oxidized the sulfur species produced and the higher the sulfide oxidation. On the contrary, high loading rate resulted in a reduction of sulfide oxidation efficiency. The results obtained in this study together with engineering calculations show that the proposed process could represent a cost-effective approach for sodium and sulfur recovery from SCS.

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## 1. Introduction

Hydrogen sulfide is a toxic, malodorous and corrosive compound. The removal of sulfide dissolved in wastewater and off-gases from chemical and petrochemical industrial activities represents a considerable cost (Maugans et al., 2010; Paulino and Alfonso, 2012; Veerabhadraiah et al., 2011). The resulting wastewater is known as spent caustic stream (SCS), named after the wasted or used caustic soda. A typical SCS contains 5–12 wt% NaOH and 0.1–4 wt%  $\text{S}^{2-}$  and can be characterized as sulfidic, cresylic or naphthenic depending on their origin and composition (Alnaizy, 2008; Veerabhadraiah et al., 2011). The high pH and sulfide toxicity of SCS limit direct biological treatment, whereas neutralization and dilution may release  $\text{H}_2\text{S}_{(\text{g})}$ . SCS is a strong reducing agent and has a high oxygen demand ( $2 \text{ mol O}_2$  per  $\text{mol HS}^-$ ) (Henshaw and Zhu, 2001), resulting in dissolved oxygen depletion.

The most commonly used methods to treat SCS involve physico-

chemical processes including wet air oxidation and incineration (Alnaizy, 2008; Veerabhadraiah et al., 2011), oxidation with oxidant agents addition, precipitation and neutralization/acidification (Tanaka and Takenaka, 1995; Sheu and Weng, 2001), electrochemical (Hariz et al., 2013; Nuñez et al., 2009; Paulino and Alfonso, 2012), biological (De Graaff et al., 2012) or bio-electrochemical processes (Zhang et al., 2013).

Despite the variety of available methods to treat SCS, the key limitations that restrict their application are cost, complexity, high consumption of chemicals, safety/handling issues (Alnaizy, 2008; Veerabhadraiah et al., 2011) and most importantly the lack of recovered product. Biological processes can alleviate some of these issues, as well as delivering hydrophilic sulfur as recovery product, but require SCS pre-treatment, biomass acclimation and sludge handling to overcome limitations imposed by high toxicity, pH and COD load. Therefore, there is a general interest in more cost-effective, energy efficient and chemical free methods such as (bio)electrochemical treatment. Several studies showed its feasibility via *in situ* production of e.g iron (Hariz et al., 2013), hypochlorous acid (Martinie et al., 2006), oxygen or other alike oxidizing

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agents, and possible coupling of sulfide removal to energy recovery (Kim and Han, 2014; Wei et al., 2012, 2013; Zhang et al., 2013). While these above mentioned studies revealed the potential and can be considered a step forward, they come with some disadvantages including sacrificial anodes, high-energy input to generate oxidizing agents and short life expectancy of materials.

Here we propose a novel method that could avoid these concerns. The method relies on the simultaneous anodic oxidization of sulfide coupled to cathodic caustic generation in a two-compartment electrochemical cell. In the anode, sulfide is oxidized to elemental sulfur and other sulfur oxyanions, while in the cathode water is reduced to hydroxide anions. In order to maintain electroneutrality, sodium from the anode migrates through a cation exchange membrane (CEM) that separates the two chambers and allows the selective migration of sodium from the anode to the cathode chamber. Key advantages of this approach would be 1) elimination of chemical dosing for sulfide oxidation and thus, less operational, transport, handling and storage cost of potentially hazardous chemicals, which reduces occupational health and safety concerns, 2) recovery of sodium and oxidized sulfur species that can be re-used *in situ* or be sold, 3) straightforward process design, 4) potentially low energy demand that can be sourced from renewable supply and 5) a neutralized stream with lower salinity and sulfide is generated towards discharge. Therefore, the overall objective of this study is to investigate the feasibility of this approach and identify the key operational aspects.

## 2. Materials and methods

### 2.1. Reactor setup and operation

#### 2.1.1. Batch-fed reactor

The electrochemical cell consisted of two parallel Perspex frames with internal dimensions of  $20 \times 5 \times 2$  cm separated by a CEM (Fumasep FKB-PK-130, Fumatech GmbH, Germany) according to (Pikaar et al., 2011). A reference electrode (Ag/AgCl (3 M KCl), ALS, Japan, + 0.210 V vs. SHE at 25 °C) was placed in the anode compartment. A flattened mesh shaped tantalum–iridium mixed metal oxide (TaO<sub>2</sub>/IrO<sub>2</sub>: 0.65/0.35) coated titanium electrode (Magneto Anodes BV, The Netherlands) with a projected surface area of 100 cm<sup>2</sup> was used as anode material. Stainless steel fine mesh (projected surface area of 100 cm<sup>2</sup>) was used as cathode (mesh width 44 μm, wire thickness: 33 μm, Solana, Belgium) and a stainless steel frame was serving as current collector. A spacer (ElectroCell Europe A/S, Tarm, Denmark) was placed between the electrodes and the CEM to prevent membrane contact with the electrodes. The batch electrochemical cell was galvanostatically controlled using a power source (type PL-3003D, Protek) at a current density of 100 A m<sup>-2</sup>.

The anolyte consisted of 4 wt% NaOH and 1 wt% Na<sub>2</sub>S–S simulating a typical SCS. The catholyte was 4 wt% NaOH at the onset of the experiment which ensured sufficient initial conductivity and avoided putative non-electrically driven diffusion of sodium across the CEM. A recirculation flow of 6 L h<sup>-1</sup> was applied to obtain sufficient mixing by a peristaltic pump (Watson-Marlow Inc., Massachusetts, US). Masterflex Norprene tubing with an internal diameter of 6 mm was used for both anolyte and catholyte and recirculation lines. H<sub>2</sub> produced in the cathode was collected in the cathode effluent bottle.

#### 2.1.2. Continuous reactor operation

The continuous-mode electrochemical cell (Fig. 1 red lines) was set up as a low-volume cell (internal dimensions of the cell compartments were  $7 \times 2 \times 1$  cm with  $5 \times 2$  cm effective membrane area). SCS of the same composition as for batch mode was used as

anolyte. The catholyte was initially 4 wt% sodium hydroxide and then distilled water was fed continuously at a flow rate of  $82 \pm 17$  mL d<sup>-1</sup> (HRT 4 h). Recirculation flow was set at 2 L h<sup>-1</sup> to provide sufficient mixing in both compartments. Peristaltic pumps (Watson-Marlow Inc., Massachusetts, US) and flows were verified daily to assure accuracy and calculate standard deviations.

Three different sets of experiments were performed. In the first one, the reactor was run in a continuous mode to determine a long-term operation performance at a fixed current density of 100 A m<sup>-2</sup>. The operation time was run in four periods: 1) day 0–25 and 35–49; the anolyte flow rate was  $128 \pm 5$  mL d<sup>-1</sup> and sulfide loading rate (SLR) of  $40 \pm 3$  g<sub>(S)</sub> L<sup>-1</sup> d<sup>-1</sup>, 2) day 25–35; anode flow rate was decreased to  $73 \pm 6$  mL d<sup>-1</sup> and SLR was  $26 \pm 2$  g<sub>(S)</sub> L<sup>-1</sup> d<sup>-1</sup>, 3) day 49–104; batch mode operation at 0.5 A m<sup>-2</sup> (reactor remains assembled) and 4) day 104–132; anolyte flow rate was increased to  $134 \pm 6$  mL d<sup>-1</sup> and SLR was  $47 \pm 2$  g<sub>(S)</sub> L<sup>-1</sup> d<sup>-1</sup>. The catholyte flow rate was kept constant at  $82 \pm 17$  mL d<sup>-1</sup>. Along with flow rates, cell voltage, sulfur species, sodium and hydroxide concentrations were monitored on a daily basis. The second experiments assessed the impact of current density on reactor performance and sulfur speciation. Experiments were run at 50, 100, 150 and 200 A m<sup>-2</sup> and the values presented herein are the ones recorded in triplicates once a new steady state was reached (typically following the 5 times the hydraulic residence time thumb rule and as long as concentrations remained constant). Anolyte and catholyte flow rates were  $121 \pm 10$  mL d<sup>-1</sup> at SLR of  $42 \pm 4$  g<sub>(S)</sub> L<sup>-1</sup> d<sup>-1</sup> and  $73 \pm 3$  mL d<sup>-1</sup> respectively. The third experiments aimed to investigate the impact of SLR - by applying different flow rates ranging from 135 to 530 mL d<sup>-1</sup>. Experiments were run at 50, 100, 150 and 200 g<sub>(S)</sub> L<sup>-1</sup> d<sup>-1</sup> at 100 A m<sup>-2</sup> and the values presented herein are the ones recorded in triplicates once a new steady state was reached. The ratio between the smallest SLR and smallest flow rate is slightly different than the ratio of the highest SLR and highest flow rate due to slight differences in HS<sup>-</sup> concentration when preparing feeding. An open circuit replicate was run to confirm that sulfide removal and NaOH recovery are only driven by the applied current. To assess whether sulfur species were crossing the membrane, catholyte samples were taken periodically.

### 2.2. Chemical analysis

Samples from the reactor were immediately preserved in previously prepared Sulfide Antioxidant Buffer solution prior to analysis as suggested by Keller-Lehmann et al. (2006). Sulfide, sulfite (SO<sub>3</sub><sup>2-</sup>) and thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) concentrations were measured by ion chromatography (IC), using an IC930 compact Metrohm IC system (Metrohm, Switzerland), according to Keller-Lehmann et al. (2006). The eluent consists of 3.5 mM Na<sub>2</sub>CO<sub>3</sub> and 3 mM NaHCO<sub>3</sub> at a flow rate of 0.8 mL min<sup>-1</sup>. A 0.1 M NaOH solution is used to produce a pH gradient needed for thiosulfate detection in the IC system. Sulfate (SO<sub>4</sub><sup>2-</sup>) was determined on an IC761 compact Metrohm IC system (Metrohm, Switzerland) equipped with a Metrosep A Supp 5–150 anion exchange column and a conductivity detector, according to Standard Methods (APHA, 1992). The eluent, consisting of 3.2 mM Na<sub>2</sub>CO<sub>3</sub> and 1 mM NaHCO<sub>3</sub>, had a flow rate of 0.7 mL min<sup>-1</sup>. To measure the polysulfide and elemental sulfur concentrations, all sulfur species were oxidized to sulfate with excess H<sub>2</sub>O<sub>2</sub> as described elsewhere (Dutta et al., 2010). The difference in sulfur equivalent between the sulfate after H<sub>2</sub>O<sub>2</sub> oxidation and other species measured before H<sub>2</sub>O<sub>2</sub> oxidation (i.e. sulfide, sulfite, thiosulfate and sulfite) was regarded as the sum of polysulfides and elemental sulfur.

Alkalinity, as indicator of NaOH concentration, is measured by titrating the cathode effluent with a 1 M HCl solution. Sodium was determined following procedures outlined in Standard Methods

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