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Electrochemical sulfide abatement in sewer systems

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School of Chemical Engineering*

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- (i) Ilje Pikaar, René A. Rozendal, Zhiguo Yuan, Jürg Keller and Korneel Rabaey. Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities. Incorporated as Appendix A. The research was conceived by IP, with contributions from RAR, KR, ZY and JK. IP, RAR and KR were responsible for the design of the experiments. IP performed the experiments. IP, RAR, KR and ZY were responsible for data interpretation. IP was responsible for drafting and writing, with contributions from RAR, KR, ZY and JK.
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Statement of Contributions by Others to the Thesis as a Whole

- (i) Dr. Beatrice Keller-Lehmann, Kar Man Leung, Susan Cooke and Ms. Jianguang Li operated Ion Chromatography (IC), High Performance Liquid Chromatography (HPLC) and Flow Injection Analyzer (FIA) to analyse dissolved sulfur species, volatile fatty acids and ammonia concentrations, respectively.
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- (ii) Ilje Pikaar, René A. Rozendal, Zhiguo Yuan, Jürg Keller and Korneel Rabaey. High rate electrochemical sulfide removal from synthetic feed and real domestic wastewater. In: 6th International Conference on Sewer Processes and Networks, 7-10 November 2010, Gold Coast, Australia.
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Abstract

Hydrogen sulfide generation in sewer networks represents a major issue in sewer management. It causes sewer corrosion, results in odour problems and its toxicity can cause health problems for sewer workers. Especially sewer corrosion is of concern as it causes severe damage to the sewer infrastructure. For example, the costs associated with sewer corrosion are in the order of \$100 million dollar annually in Australia alone (private communication with Water Services Association of Australia). Existing strategies to prevent sewer corrosion are considered expensive as they normally involve the continuous dosing (i.e. 24 hours a day and 7 days a week) of significant amounts of chemicals.

In view of the practical limitations of existing strategies there is an urgent need for alternative sulfide abatement strategies. Recent advances in electrode development and operation have stimulated an interest in electrochemical techniques for the remediation of sulfide from wastewater. Electrochemical techniques offer several advantages over existing technologies as they do not require dosing, transport and storage of hazardous chemicals, all of which constitute serious occupational health and safety hazards. Therefore, this thesis aimed to develop and demonstrate the working principle of a novel technology using an electrochemical cell for sulfide abatement in sewer systems. Several electrochemical approaches, either based on anodic reactions (i.e. direct and indirect sulfide oxidation by in-situ generated oxygen) or cathodic reactions (i.e. hydrogen peroxide or caustic generation), were investigated.

At the anode side, it was established that direct oxidation of sulfide was not feasible, due to the low sulfide concentrations normally present in sewage. The results also showed that independent of the electrode materials used, namely, Ta/Ir, Ru/Ir, Pt/Ir, PbO₂ and SnO₂ coated titanium, oxidation occurred mainly indirectly via electrogenerated oxygen. Furthermore, elevated chloride concentrations, often observed in coastal areas, did not entail any significant difference in performance. The long-term performance of electrochemical sulfide removal under real sewer conditions was investigated during field trials. Sulfide could be removed to concentrations below 1 mg L⁻¹ at average sulfide removal efficiencies above 80% over a period of ~4 months, after a residence time through a simulated rising main. At the cathode side, it was shown that caustic can be generated from sewage. Over time, the cell voltage increased due to an increase in resistance of the system caused by membrane fouling due to precipitation of calcium and magnesium. Therefore, a method, based on periodic polarity switching of the electrodes, was developed to control this membrane fouling.

Overall, the results showed that electrochemical caustic generation from sewage was the most cost-effective sulfide abatement strategy. The produced caustic can be periodically dosed to deactivate the sulfate reducing bacteria present in the sewer biofilm responsible for sewer corrosion. Based on the current efficiency obtained in this thesis and cell voltage applied, our cost calculation showed that the costs for sulfide abatement can be reduced from AUS \$2.5-9.4 kg S⁻¹ to AUS \$0.83-1.17 kg S⁻¹. The results obtained in this thesis clearly show the economic potential of in-situ generation of caustic from sewage. However, to get to a mature technology at full scale, several process and engineering aspects have to be solved. In addition, the long-term performance at larger scale under real sewer conditions is needed to validate the most important process parameters in order to accurately assess the costs of this promising technique.

Keywords

sewer corrosion, electrochemical systems, hydrogen sulfide, oxygen, caustic, polarity switching, zero-chemical.

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List of abbreviations

AC	Activated carbon
AEM	Anion exchange membrane
AO	Anthraquinone oxidation
BOD	Biological oxygen demand
BPM	Bipolar membrane
CE	Coulombic efficiency or charge transfer efficiency
CEM	Cation exchange membrane
CMM	Charge mosaic membranes
COD	Chemical oxygen demand
CV	Cyclic voltammetry
DMS	Dimethyl sulfide
DMSO	Dimethyl sulfoxide
DO	Dissolved oxygen
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental protection agency
FIA	Flow injection analysis
GC	Gas chromatography
GDE	Gas diffusion electrode
HPLC	High performance liquid chromatography
HRT	Hydraulic retention time
IC	Ion chromatography
ICP-OES	Inductively coupled plasma optical emission spectrometry
IEM	Ion exchange membrane
LEL	Lower explosive limit
MFC	Microbial fuel cell
MMO	Mixed metal oxide
OH&S	Occupational health & safety
PTFE	Polytetrafluoroethylene
SAOB	Sulfide anti oxidizing buffer
SHE	Standard hydrogen electrode
SOB	Sulfide oxidizing bacteria

SRB	Sulfate reducing bacteria
TKN	Total kjeldahl nitrogen
TOC	Total organic carbon
VFA	Volatile fatty acids
VGCF	Vapor grown carbon fibre
WWTP	Wastewater treatment plant
XRF	X-ray fluorescence

1. Introduction

1.1 Background

Wastewater originating from households and industrial activities, as well as run-off water from precipitation in urban areas, is normally collected and transported via sewers to a wastewater treatment plant (WWTP) for treatment and ultimate disposal into surface waters. Sewers are often complex systems consisting of a large amount of individual pipes, inlet structures and pumps. The wastewater is either transported by means of gravity (i.e. gravity sewers), or by the use of pumps (i.e. rising mains). In gravity sewers, the sewer pipe is normally only partially filled, whereas rising mains are completely filled.

The conditions in sewer systems fluctuate depending on rainfall and diurnal inflow variations. During dry weather conditions the hydraulic flow follows the behaviour of the community, which results in a typical daily (day-night) variability in hydraulic flow of a factor 10. In sewers receiving both domestic wastewater and run-off water (i.e. combined sewer systems) the hydraulic load can increase by a factor of 100-1000 during heavy rainfall events, depending on the local situation [1]. A lot of effort has been dedicated to the development of sewer systems, procedures for design, and operation under these high hydraulic loads [1]. Under these conditions, chemical and biological processes (e.g. hydrolysis, fermentation and hydrogen sulfide generation) play only a minor role. However, these chemical and biological processes become important during dry weather conditions, which constitute about 95% of the time. A biological process with serious implications for sewer systems is the formation of hydrogen sulfide by the reduction of sulfate by sulfate reducing bacteria (SRB) under anaerobic conditions in the biofilm of the sewer walls. Emission of this hydrogen sulfide from the liquid phase to the headspace in the gravity sections of sewers results in sewer corrosion and odour and health problems [2].

Concrete corrosion causes severe damage to sewer pipes and structures like pumping stations. This has an enormous economic impact due to the need for counteractive measures and replacement or repair of existing sewer systems [3, 4]. The cost of remediation or replacement of corroded sewer pipes is in the order of several hundreds to thousands of dollars per meter, depending on the diameter, location and depth of the sewer pipe [5]. Sydney *et al.* (1996) reported that approximately 10% of the sewer infrastructure in Los Angeles County is subject to significant sulfide corrosion, resulting in an estimated cost of US\$400 million for rehabilitation of the sewer network [6]. In Flanders (a part of Belgium),

annual costs due to concrete corrosion is estimated at €5 million, being 10 % of the total annual costs for the wastewater collection and treatment [7]. Rehabilitating damaged sewer networks in Germany is estimated at €100 million per year [8]. In Australia, the costs associated with sewer corrosion are in the order of AUS\$100 million dollar annually (private communication with Water Services Association of Australia). This shows that concrete corrosion of sewer pipes is a serious problem globally.

Existing abatement strategies normally involve the continuous dosing of chemicals to prevent sulfide formation, oxidize formed sulfide, or prevent its transformation from liquid to the gas phase. These strategies are considered expensive (US\$1.7-7.2 kg S⁻¹) [2] as they typically require significant amounts of chemicals that need to be dosed continuously (24 hours a day and 7 days a week). Furthermore, they come with a number of limitations such as COD loss and the necessity for transport and storage of chemicals. Additionally, the transport, handling and storage of chemicals also constitute serious occupational and safety hazards.

1.2 Thesis objectives

In view of the practical limitations of existing strategies, there is a general interest in alternative sulfide abatement technologies. Recent advances in electrode development and operation have stimulated an interest in electrochemical sulfide abatement strategies for its remediation from wastewater. Electrochemical techniques offer several advantages over existing technologies as they do not require dosing, transport and storage of potentially hazardous chemicals. Moreover, electrochemical techniques are robust, versatile, controllable and hence amenable to automation. Recently, removal of sulfide from industrial wastewater using an electrochemical approach by direct oxidation to sulfur at the electrode surface was suggested [9, 10]. Although preliminary testing suggested its suitability, the concept of electrochemical sulfide oxidation has not yet been tested on real domestic wastewater, let alone in sewer systems. Therefore, the objective of this PhD thesis is to investigate the feasibility of electrochemical sulfide control in (domestic) sewer systems to prevent sewer corrosion. Due to its ease of operation and lack of peripherals this electrochemical approach is expected to exhibit important advantages compared to existing technologies.

1.3 Organization of the thesis

This thesis is divided into five chapters and five appendices. In chapter 2, the sulfur chemistry, processes behind sewer corrosion and the principles and fundamentals of electrochemistry are discussed. In addition, this chapter also gives a thorough literature review about the state of the art of sulfide abatement in sewer systems. In chapter 3, the thesis objectives and research methodology are discussed in detail. In chapter 4, the main research outcomes are described. Finally, chapter 5 describes the conclusions, perspectives and opportunities for electrochemical techniques for sulfide abatement with recommendations for future work in this direction. The five appendices describe the detailed experimental studies of the different research objectives. Appendix A describes the ‘Electrochemical oxidation of sulfide from synthetic feed and real domestic wastewater at high current densities’. Appendix B describes the ‘Electrochemical sulfide oxidation from domestic wastewater using mixed metal coated titanium Electrodes’. In Appendix C the working principle of ‘Electrochemical caustic generation from sewage’ is presented. Appendix D reports on the ‘Long-term field test of an electrochemical method for sulfide removal from sewage’. Lastly, Appendix E shows the experimental methodology and results of cathodic hydrogen peroxide generation using carbon catalysed gas diffusion electrodes.

2. Literature Review

2.1 Sulfur chemistry

2.1.1 The global sulfur cycle

Sulfur is a critical component of our blood plasma, an essential component for many proteins and therefore essential for life. Sulfur is a multivalent non-metal element and can be present in many different forms in valence states ranging from +6 in sulfate to -2 in sulfide (see Table 2.1). In nature, solid sulfur is mostly present in the most reduced states (-1 or -2) in metal or metalloid sulfides (e.g. pyrite (FeS_2), Pyrrhotite ($\text{Fe}_7\text{S}_8\text{-FeS}$) and Gelena (PbS)) or in the most oxidized state (+6) in Gypsum (CaSO_4) [11]. In addition, it can also be present as elemental sulfur (0) and in organic matter. There are a variety of natural sources and human activities that lead to the emission of sulfur into the atmosphere. Natural sources include volcanic eruptions and the breakdown of organic materials in swamps and tidal flats. Human activities that result in the emission of sulfur (usually as gaseous SO_2) include the burning of fossil fuels and the smelting of sulfide ores. Since many of the sulfur species are soluble, considerable amounts of sulfur can be present in groundwater, oceans, rivers and other surface waters, depending on local geological conditions [12].

Table 2.1. Oxidation states of sulfur in common compounds (adapted from [13])

Compounds	Oxidation State
Hydrogen sulfide (H_2S), Hydrogen sulfide ion (HS^-) Sulfide ion (S^{2-})	-2
Disulfane (H_2S_2) , disulfide (S_2^{2-}) Polysulfide, (S_n^{2-})	-1 -2/n
Elemental sulfur (S_n) , Organic polysulfane ($\text{R-S}_n\text{-R}$) Dichlorodisulfane (Cl-S-S-Cl)	0 +1
Sulfur dichloride (SCl_2), sulfoxylate (SO_2^{2-}), thiosulfate ($\text{S}_2\text{O}_3^{2-}$) Tetrathionate ($\text{S}_4\text{O}_6^{2-}$)	+2 +2.5
Dithionate ($\text{S}_2\text{O}_4^{2-}$) Sulfur dioxide (SO_2), sulfite (SO_3^{2-})	+3 +4
Dithionate ($\text{S}_2\text{O}_6^{2-}$) , sulfonate (RSO_3^-) Sulfate (SO_4^{2-}), sulfur trioxide (SO_3), peroxosulfate (SO_5^{2-})	+5 +6

2.1.2 The biological and sewer sulfur cycle

The biological sulfur cycle involves the biochemical oxidation and reduction of several sulfur species. The most important processes are the reduction of sulfate and elemental sulfur to sulfide, the oxidation of sulfide to elemental sulfur and sulfate, the oxidation of sulfur to sulfate and the degradation of organic material containing sulfide which results in the release of sulfide, by different micro-organisms. In Table 2.2 an overview of the key processes and the prokaryotes involved in the biological sulfur cycle is presented.

Table 2.2. Key processes and prokaryotes of the geochemical sulfur cycle.

Process	reaction	Organisms
Sulfide/sulfur oxidation	$\text{H}_2\text{S} \rightarrow \text{S}^0 \rightarrow \text{SO}_4^{2-}$	
Aerobic		Sulfur chemolithotrophs (<i>e.g. Thiobacillus, Beggiatoa and many others</i>)
Anaerobic		Purple and green phototrophic bacteria, some chemolithotrophs
Sulfate reduction	$\text{SO}_4^{2-} \rightarrow \text{H}_2\text{S}$	
Anaerobic		Sulfate reducing bacteria (<i>e.g. Desulfovibrio, Desulfobacter</i>)
Sulfur reduction	$\text{S}^0 \rightarrow \text{H}_2\text{S}$	
Anaerobic		<i>Desulfuromonas</i> , many hyperthermophilic Archaea
Sulfur disproportionation	$\text{S}_2\text{O}_3^{2-} \rightarrow \text{H}_2\text{S} + \text{SO}_4^{2-}$	
Anaerobic		<i>Desulfovibrio</i> , and others
Organic sulfur compound oxidation	$\text{CH}_3\text{SH} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$	
(An)aerobic		Many organisms are able to do this
Organic sulfur compound reduction	$\text{DMSO}^{\text{a)}} \rightarrow \text{DMS}^{\text{b)}}}$	
(An)aerobic		Many organisms are able to do this
Desulfurylation	$\text{organic-S} \rightarrow \text{H}_2\text{S}$	
Anaerobic		Many organisms are able to do this

a) DMSO: dimethyl sulfoxide

b) DMS: methyl sulfide

In Figure 2.1 a schematic overview of the sulfur cycle in sewer networks is presented. For sewage, the main source of sulfur is sulfate in a typical concentration range of 13–67 mg L⁻¹ SO₄²⁻-S [14-16]. Normally, fresh sewage does not contain any hydrogen sulfide. Hydrogen

sulfide generation is the result of the reduction of sulfate by sulfate reducing bacteria (SRB) under anaerobic conditions. This process mainly takes places in the inner parts of the biofilms and sediments of the sewer pipes [17]:

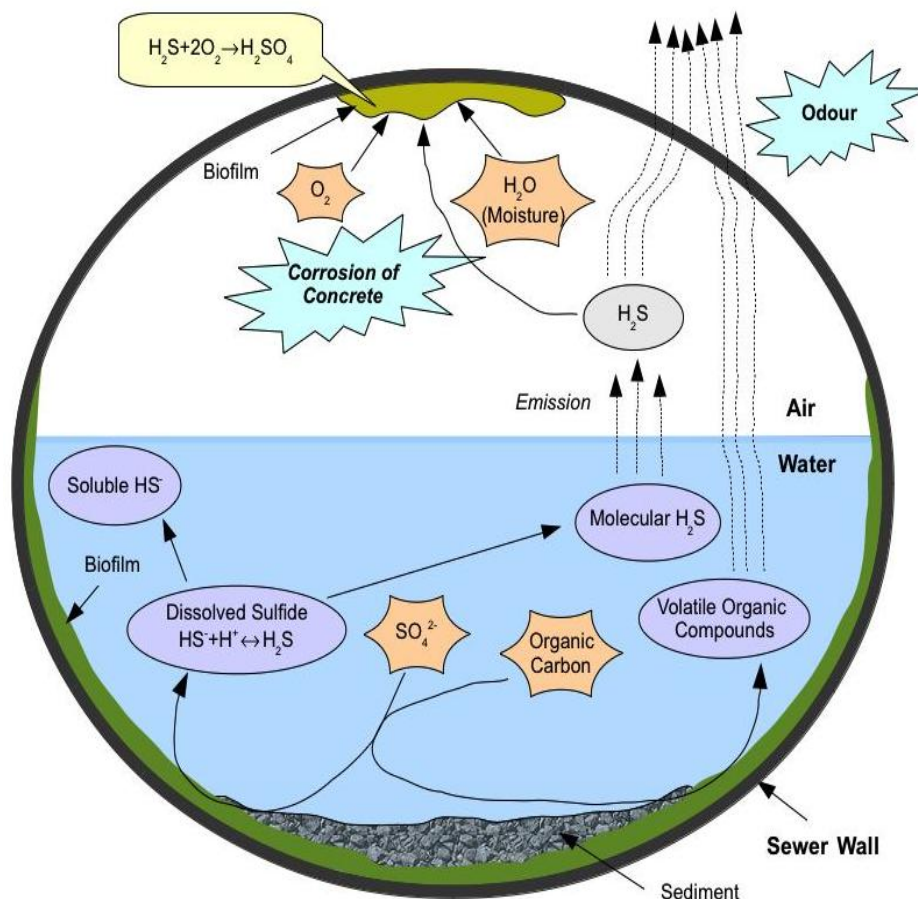


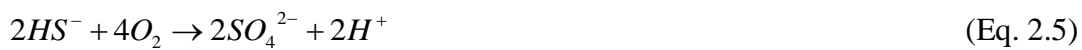
Figure 2.1. Schematic overview of the sulfur cycle in sewer networks

SRB are widespread in aquatic systems, and are well described in literature [18]. Generally, SRB are obligate anaerobes that reduce sulfate to sulfide. SRB often are also capable of reducing thiosulfate, sulfur, and sulfite. SRB can utilize several electron donors such as hydrogen, formate, acetate, propionate, ethanol and long chain fatty acids, and they can co-exist or even form symbiotic relationships with other bacteria. The latter is important as this is the case in sewer systems. There are many factors in sewers that influence the rate at which sulfate is reduced to sulfide. The main conditions that cause and accelerate sulfide production are (i) high BOD concentrations (electron-donating substrate for SRB bacteria), (ii) elevated wastewater temperatures, (iii) high sulfate concentrations (e.g. due to seawater ingress), (iv)

long hydraulic retention times (HRT), (v) the number of pumping stations and the length of rising mains (i.e. anaerobic conditions) and (vi) sewer debris [5].

In the presence of oxygen, hydrogen sulfide can be oxidized to elemental sulfur, thiosulfate and sulfate by sulfide oxidizing bacteria (SOB) [19]. Sulfide and sulfur oxidizing bacteria (SOB) are mainly chemolitotrophic or phototrophic. With respect to sewer networks, only chemolitotrophic SOB are important due to the absence of sunlight. In sewer networks in the presence of oxygen, sulfide is normally oxidised biologically by SOB to sulfur, thiosulfate and sulfate [20]. This biological sulfide oxidation mainly takes place in the aerobic layer of the biofilm of the sewer walls [21]. Sulfur disproportionation, desulfurylation and organic sulfur compound oxidation and reduction are biological processes that are less important in sewer networks.

In addition to biological oxidation and reduction reactions, the emission of hydrogen sulfide from the water to the gas phase and abiotic sulfide oxidation with oxygen are important processes in sewer systems. Abiotic oxidation of sulfide anions with oxygen is a complex process whereby several reaction products can be formed including sulfur, sulfite, thiosulfate and sulfate:



The type of product formed during abiotic sulfide oxidation depends on the pH, the presence of heavy metals (i.e. catalyst) and the sulfide and dissolved oxygen concentration [22, 23]. For example, Chen and Morris found that the oxidation rate is very slow at pH values below 6 and increases significantly at pH > 7 with a maximum rate observed at pH 8 [24]. A further increase in pH results in a minimum oxidation rate at pH 9 after which it increases again to a second maximum near a pH of 11 and finally decreases again in more alkaline solutions. The oxidation of hydrogen sulfide by oxygen proceeds slowly in the absence of catalysts because of the high activation energy required for sulfide oxidation. Transition metals ions such as

nickel, zinc, molybdenum and iron and metal complexes (e.g. cobalt phthalocyanine and cobalt(II)4,4',4'',4'''-tetrasulfophthalocyanide) are usually effective catalysts for sulfide oxidation since they are capable of changing the electronic structure of hydrogen or oxygen [25]. As a result, the activation energy barrier imposed on the reaction by spin-state symmetry restrictions is lowered. Indeed, several studies showed the catalytic effect of metals (e.g. nickel, zinc, molybdenum and iron) during the auto-oxidation of sulfide [26-29]. Heavy metals such as iron and zinc are often present in low concentrations in sewage [30] and might thus enhance aerobic chemical sulfide oxidation. For example, the addition of Fe(III) in moderate concentrations (i.e. $< 5 \text{ mg L}^{-1}$) significantly increased the chemical sulfide oxidation rate in addition to sulfide precipitation [31].

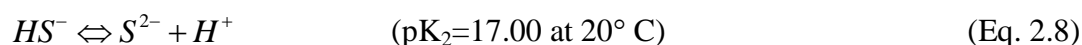
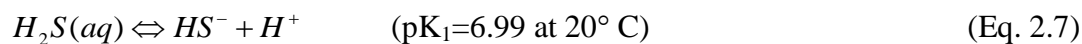
There has been some speculation over the relative importance of chemical and biological sulfide oxidation in sewer networks. Nielsen *et al.* (2006) found that sulfide oxidation by biofilms in batch tests accounted for more than 95% of the total sulfide oxidation [21]. Wilmot *et al.* (1988) found biological sulfide oxidation to account for only 12-56% of the total sulfide oxidized using settled raw wastewater or primary effluent [22]. Kotronarou *et al.* (1991) found that the sulfide oxidation rate of autoclaved wastewater was just 30% of that of active wastewater [25]. Guiterrez *et al.* (2008) found similar contributions of chemical and biological sulfide oxidation from domestic wastewater during laboratory scale experiments [32]. Hence, the above-mentioned studies show that both chemical and biological sulfide oxidation reactions are generally significant in sewers. Their relative importance will mainly depend on the biofilm structure, the sewer diameter (i.e. the smaller the diameter the higher the wall surface area to volume ratio), the temperature, and the presence of catalysts. In addition, temporal and spatial fluctuations in both the biological and chemical sulfide oxidation can be expected due to the dynamic behaviour of wastewater composition and hydraulics in sewer systems.

2.1.3 Properties of sulfur species

2.1.3.1 Hydrogen sulfide and polysulfide

Hydrogen sulfide is present in several industrial waste streams originating from tanneries, paper mills, oil refineries, petroleum plants, viscose rayon manufacturers and abattoirs. In addition, hydrogen sulfide is present in certain types of natural gas, sewage, waste gas originating from different industries (e.g. petroleum plants) as well as in volcanic exhalations

and water exiting from hydrothermal vents on the ocean floor. Furthermore, it is formed in huge quantities during the desulfurization of crude oil carried out by refineries. Hydrogen sulfide in solution is a weak acid and dissociates according to [13]:



There is some speculation in the literature about the exact value for the pK_2 with values ranging from 11.96 to 17.00 [13]. However, considering that in sewage the pH normally is within the range of pH 6.5-8.0, it rules out the existence of S^{2-} independent of the pK_2 value used. Therefore, for sulfide present in sewage only the first dissociation reaction of H_2S is of importance. Figure 2.2. shows the distribution of H_2S , HS^- and S^{2-} as function of the pH. H_2S is moderately soluble in water, ranging between 3000 and 4000 mg L^{-1} at atmospheric pressure and normal temperatures found in wastewater [33].

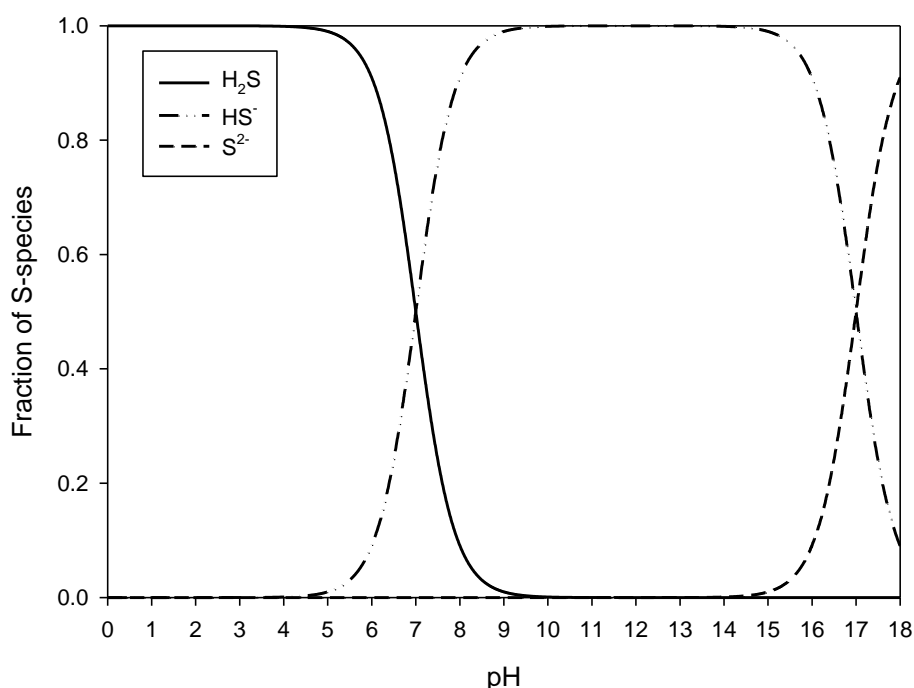


Figure 2.2. Distribution of sulfur species as function of the pH

The second category of sulfides concerns polysulfides, which are unbranched chains of sulfur atoms, related to the polysulfanes (H_2S_x). The acidity constants of polysulfanes are so low

that polysulfide can be assumed to be unprotonated [13]. Polysulfides can be formed from the reaction of sulfide with elemental sulfur and are characterized by their yellowish colour when in solution:



The chain length can differ from 2 to 9, but at moderate alkaline conditions polysulfides with chain lengths of $x = 4, 5, 6$ are the dominant species whereas the shorter polysulfide chains (i.e. $x = 2$ and 3) are only observed at strongly alkaline conditions, i.e. $\text{pH} > 14$ [34]. Under acidic conditions polysulfides are not stable and can therefore only exist in water at $\text{pH} > 6$ [13].

2.1.3.2 Elemental sulfur

Elemental sulfur (S^0) is a soft bright yellow crystalline solid. Sulfur has more than 30 different solid chemical forms (allotropes), which is more than any other element [13]. At ambient temperature and pressure, most of the allotropes consist of cyclic non-polar molecules (rings) of different sizes (S_n), while some exist as polymeric chains of high molecular mass (S_μ). All of these allotropes are hydrophobic and therefore have low solubility in water (i.e. $5 \mu\text{g L}^{-1}$) [35]. The most thermodynamically stable form of elemental sulfur is orthorhombic α - S_8 , and is therefore the main constituent of commercial sulfur. Elemental sulfur is normally produced as a by-product in the petroleum industry during oil refining and natural gas processing. The main commercial use of elemental sulfur is in fertilizers (i.e. 96%), but it is also used for matches, gunpowder and pesticides. Sulfur can also be produced biologically by phototrophic or aerobic bacteria [36]. Contrarily to chemically produced sulfur, biological sulfur is hydrophilic and dispersible in water [36]. A shortage of sulfur is not expected in the short term as the reserves of sulfur in crude oil, natural gas and ores is still large. However, in the long-term alternative sources for sulfur such as that produced biologically are required as crude oil, natural gas and ores are non-renewable sources. In this perspective, sulfur recovery from industrial wastewater using an electrochemical cell has been proposed recently [10].

2.1.3.3 Sulfate, thiosulfate and sulfite

Sulfate is widely present in dissolved form in marine and freshwater environments, domestic sewage and in several industrial wastewater streams. It is also ubiquitous as an insoluble salt in several minerals such as gypsum (CaSO_4) and barite (BaSO_4) [13]. It is the most oxidized sulfur form and therefore also stable in the presence of oxidizing agents. Sulfate concentrations in domestic sewage are typically in the range of 10-30 mg S L⁻¹ (e.g. originating from the use of alum ($\text{Al}_2(\text{SO}_4)_3$) in the water treatment processes) but can be particularly elevated in cases where there is infiltration of seawater. Other soluble sulfur oxyanions that can be found in aqueous solutions are thiosulfate ($\text{S}_2\text{O}_3^{2-}$), sulfite (SO_3^{2-}), dithionate ($\text{S}_2\text{O}_4^{2-}$) and tetrathionate ($\text{S}_4\text{O}_6^{2-}$) [13].

2.1.3.4 Organic sulfur compounds

Although sulfide is the major inorganic source of sulfide in sewers, there are many other odorous substances in addition to sulfide. An overview of these odorous substances is given in Table 2.3.

Table 2.3. Odorous compounds in wastewater (adapted from [5])

Name	Formula	Characteristic odour	Detection threshold (ppm)
Hydrogen sulfide	H_2S	Rotten eggs	0.0005
Methylamine	CH_3NH_2	Putrid, fishy	4.7
Allyl mercaptan	$\text{CH}_2\text{CHCH}_2\text{SH}$	Disagreeable garlic	0.0001
Amyl mercaptan	$\text{CH}_3(\text{CH}_2)_4\text{SH}$	Unpleasant, putrid	0.0003
Benzyl mercaptan	$\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	Unpleasant, strong	0.0002
Ethyl mercaptan	$\text{CH}_3\text{CH}_2\text{SH}$	Decayed cabbage	0.0003
Dimethyl sulfide	$(\text{CH}_3)_2\text{S}$	Decayed cabbage	0.001
Sulfur dioxide	SO_2	Pungent, irritating	2.7
Methyl mercaptan	CH_3SH	Decayed cabbage	0.0005
Thiocresol	$\text{CH}_3\text{C}_6\text{H}_4\text{SH}$	Skunk, irritating	0.0001
Thiobismethane	CH_3SCH_3	Rotting meat	0.0011

These compounds, which often contain a sulfur atom, are generated as a result of microbiological breakdown of proteins and amino acids and are generally highly volatile [5]. Therefore they enter the headspace of the gravity sewers where they cause odour problems.

2.1.4 Potential-pH relationship of sulfur species

E_h -pH diagrams (Pourbaix diagrams) are used to visualize the thermodynamic stability of an element in an aqueous system. Stability areas are presented as a function of pH and electrochemical potential. The electrochemical potential scale is normally characterized versus Standard Hydrogen Electrode (SHE). Figure 2.3 shows the Pourbaix diagram of the sulfur-water system at 25 °C [37]. It is important to note that the Pourbaix diagram describes the thermodynamic stability of different sulfur species in the aqueous system, but it does not provide any information about the kinetics of the reaction.

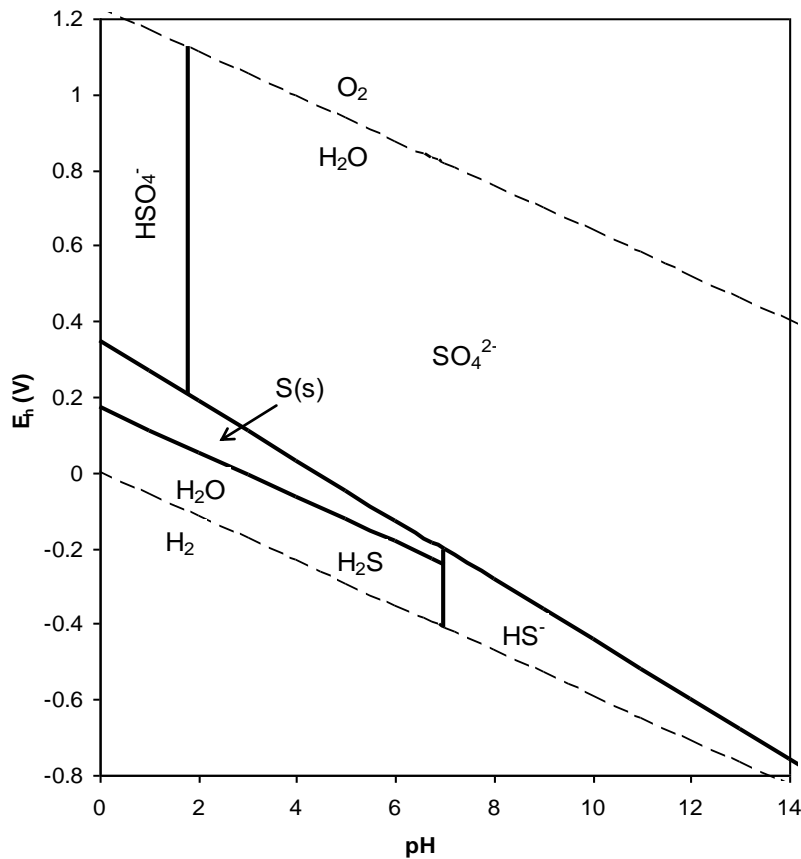


Figure 2.3. Potential (E_h) - pH diagram for the S- H_2O system at 25 °C, at standard hydrogen and oxygen pressures of 1 bar, $\Sigma S = 0.1M$, adapted from [37].

As shown in Figure 2.3 chemical elemental sulfur is only thermodynamically stable in a very small triangular domain in the presence of water and acid solutions free from oxidizing agents. At lower potentials and alkaline solutions, sulfur is considered to disproportionate to H_2S , HS^- and S_x^{2-} and SO_4^{2-} . However, in practice the kinetics of these reactions are very slow and only take place under hot and very alkaline conditions [37]. Other sulfur species

such as $S_2O_3^{2-}$, SO_3^{2-} , $S_2O_4^{2-}$, $S_4O_6^{2-}$ and polysulfides are considered to form false equilibria in aqueous solution and are therefore not shown in Figure 2.3.

2.1.5 Sulfide emission and Henry's law

Emission of H_2S from the water to the gas phase takes place in sewer sections that are only partly filled with water (e.g. gravity sewer, pumping stations, wet wells and manholes). The hydrogen sulfide in the headspace can subsequently be biologically oxidized to sulfuric acid, causing corrosion problems. This process will be discussed in detail in section 2.2. As sulfide is mainly present as HS^- and H_2S under normal conditions found in sewer networks, its dissociation can be described as follows:

$$\log \frac{[HS^-]}{[H_2S(aq)]} \equiv pH - pK_a \quad (\text{Eq. 2.10})$$

Under equilibrium conditions the emission of H_2S (aq) to the gas phase can be described by Henry's Law:

$$H_{c,H_2S} \equiv \frac{H_{H_2S}}{RT} \equiv \frac{C_{A,H_2S}}{C_{S,H_2S}} \quad (\text{Eq. 2.11})$$

Where H_{c,H_2S} is the dimensionless Henry's Law constant for hydrogen sulfide (-), H_{H_2S} the Henry's Law constant for H_2S ($L \text{ atm mol}^{-1}$), R the universal gas constant $8.314 \text{ (J K}^{-1} \text{ mol}^{-1})$, T the temperature (K), C_{A,H_2S} the H_2S concentration in the air phase ($g \text{ m}^{-3}$) and C_{S,H_2S} the saturation concentration of H_2S in the water phase at equilibrium with the air phase ($g \text{ m}^{-3}$). However, under sewer conditions, non equilibrium conditions between the water phase and the air-phase are normally obtained. Therefore, in order to quantify the emission of hydrogen sulfide to the gas phase, the mass transfer concept must be taken into account. The emission of sulfide under non-equilibrium conditions can be described as follows [38]:

$$R_{H_2S} = \frac{dC_w}{dt} = fK_L a_{H_2S} \left(C_w - \frac{C_{A,H_2S}}{fH_{c,H_2S}} \right) \quad (\text{Eq. 2.12})$$

where R_{H_2S} is the emission rate ($g\ S\ m^{-3}\ h^{-1}$), C_w the dissolved sulfide concentration in the liquid phase ($g\ m^{-3}$), f as the ratio of H_2S (aq) to total sulfide present (-) and $K_{La_{H_2S}}$ the sulfide overall mass-transfer coefficient (h^{-1}). The mass transfer resistance of sulfide is determined by several chemical and physical parameters [39] and mainly caused by the resistance of the water film (i.e. > 98%) [40]. Chemical factors contributing to the resistance include the temperature, wastewater constituents and characteristics of the sewer atmosphere (moisture content and movement of the overlaying gas phase). The most important and critical physical parameter in sewer systems is turbulence causing splashing and hydraulic outfalls, generating water droplets which dramatically increase the mass transfer constant (K_{La}) and thus the emission of sulfide to the headspace of the sewer pipe [5].

Hydrogen sulfide does not only cause sewer corrosion but also often causes odour problems (i.e. typical rotten egg smell) and occupational health and safety (OH&S) issues for sewer workers [41, 42]. Hydrogen sulfide is a toxic gas with an extremely low odour threshold, of approximately 0.5 ppb [43]. Elevated hydrogen sulfide concentrations are often observed in manholes, the headspace of gravity sewers, wet wells and pumping stations where it poses a risk for maintenance personnel [5]. Hydrogen sulfide has a higher density than air and therefore tends to accumulate at the bottom of manholes and pumping stations. At concentrations higher than 100 ppm, the human olfactory system is affected making it impossible for humans to sense the typical rotten egg smell. Consequently, maintenance personnel entering manholes may not be aware of the danger of lethal concentrations. Indeed, there are reports of a number of fatal accidents as result of lethal hydrogen sulfide concentrations [44]. For example, more than 29 hydrogen sulfide related deaths occurred in the United States between 1983 and 1992 [45]. The human toxicity of H_2S is well documented, and is presented in Table 2.4.

Table 2.4 Health effects associated with the release of H_2S

H_2S concentration (ppm)	Health effects
0.005-1	Rotten egg smell, odour complaints
10	Occupational exposure limit for 8 hours (EPA)
20	Self-contained breathing apparatus required
100	May cause headache/nausea, sense of smell lost in 2-15 minutes
200	Rapid loss of smell, burning eyes and throat
500	Loss of reasoning and balance, respiratory distress
700	Immediate unconsciousness, seizures

2.2 Biogenic corrosion in sewer systems

As discussed in paragraph 2.1.5, hydrogen sulfide can partition into the headspace of sewer pipes. The crown of the pipes is normally covered with condensate containing sufficient supplies of carbon dioxide (CO₂) and oxygen (O₂). This allows the existence of micro-organisms capable of oxidizing hydrogen sulfide at these places [46-48]. These sulfur oxidizing bacteria (SOB) oxidize sulfide with oxygen to sulfuric acid [49, 50]:



The generated sulfuric acid subsequently reacts with the alkaline components of the concrete sewer wall, resulting in degradation of the concrete [51, 52]. The process of biogenic corrosion of concrete sewer pipes can be divided into different stages. In each of these stages, different types of *Thiobacillus* species are involved [53]. At first, weak acidophilic species like *Thiobacillus intermedius* and *Thiobacillus neapolitanus* together with other bacteria will start to grow on the concrete surface. As result of their activities the pH of the alkaline sewer walls decreases. When the pH of the sewer wall drops below 5, *Thiobacillus thiooxidans* starts to grow, resulting in the production of sulfuric acid. As a result, the pH of the sewer walls can locally drop to pH values as low as 0-1. The sulfuric acid reacts with the cement of the concrete, which binds the sand and the aggregate, to form a layer of gypsum (CaSO₄) on the concrete [3]:



The thickness of this gypsum layer increases over time as more acid is produced until the cement loses its strength. Gypsum weakens the structure of the cement because it is more voluminous than cement. In addition, it can react with tri-calcium aluminates (C3A) to form ettringite (3CaO•Al₂O₃•CaSO₄•12H₂O or 3CaO•Al₂O₃•3CaSO₄•31H₂O) [3]. Ettringite is even more voluminous than gypsum and causes internal cracking and pitting, deteriorating the concrete matrix even further. Eventually, this can lead to a complete collapse of the sewer pipe [54]. The rate at which the deterioration of the sewer pipes occurs depends on several factors including the (i) hydrogen sulfide concentration, (ii) moisture content, (iii) presence of hydrocarbons, (iv) temperature, (v) (natural) ventilation rate and (vi) specific surface area of

the concrete. Problems with biogenic sewer corrosion can already occur at hydrogen sulfide concentrations as low as $0.1\text{--}0.5\text{ mg L}^{-1}$, whereas severe sewer corrosion may already occur at concentrations of 2 mg L^{-1} and higher [55]. The US EPA (1991) reported concrete corrosion rates in sewer systems of $2.5\text{--}10\text{ mm year}^{-1}$ based on an investigation of 34 cities [56]. Other studies showed an average corrosion rate of approximately $1\text{--}5\text{ mm year}^{-1}$ [7, 56-61].

2.3 State of the art of sewer corrosion abatement

Current abatement strategies are normally based on (i) the inhibition of hydrogen sulfide generation, (ii) the removal of any sulfide formed, or (iii) the prevention of the reaction of sulfuric acid with the sewer wall by the use of corrosion resistant coatings. These strategies normally involve the addition of significant amounts of chemicals as continuous dosing is often necessary. An overview of the current sulfide abatement strategies in sewer networks is presented in Figure 2.4. These techniques will be discussed in detail in the following sections.

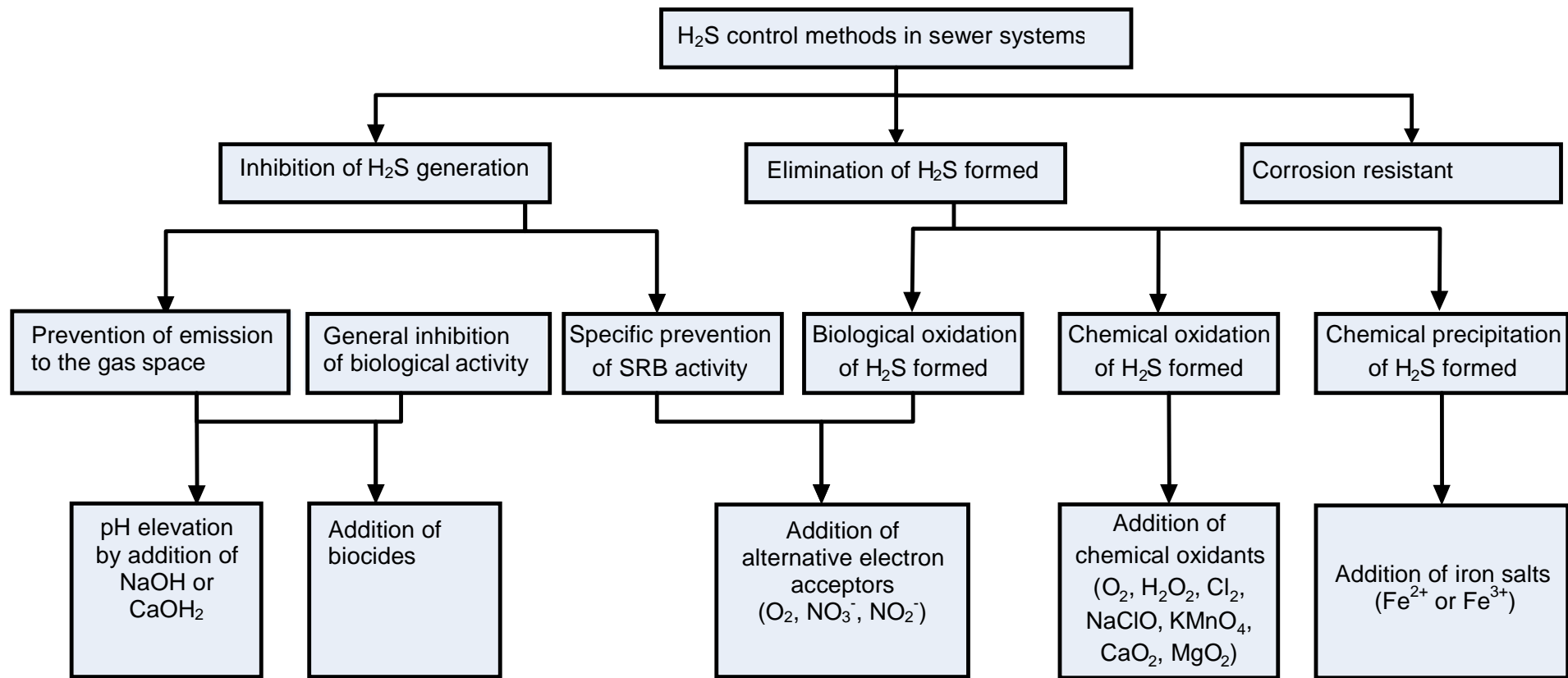


Figure 2.4 Overview currently used sulfide control measures in sewer systems (adapted from [2]).

2.3.1 Inhibition of H₂S generation

2.3.1.1 General inhibition of biological activity

pH elevation

Caustic dosing to produce elevated pH levels for a short period of time can be used to deactivate/kill the biofilm (including the SRB) present on the sewer wall. In this way, sulfide generation can be inhibited for between two days and several weeks, depending on the temperature, slime layer thickness, sulfate concentration and the pH of the sewerage [5, 62]. There is some speculation in the literature about the required hydraulic retention time and desired pH level. For example, in a study of US EPA (1991) the wastewater was elevated to a pH of 12-13 for only 20-30 minutes [56]. Recently, in a field study of Sydney Water, sulfide generation was successfully inhibited for several weeks after pH elevating the pH to a pH of 11 for 6 hours [63]. A recent industrial survey revealed that pH shock-loading is a method often used by the Australian water industry [64]. Although it is a commonly used method, there is not much known about the importance of pH and exposure time of the biofilm on the efficiency of caustic shock dosing. Recently, in a study of Sudarjanto *et al.* (2011) the impact of the pH level and contact time (i.e. HRT) on the inactivation/killing of the SRB was investigated [65]. In this study, the biofilm of several laboratory scale reactors was analysed by dead/life staining after exposure to different pH levels and HRT. The results indicated that a pH of 10.5 for 2 hours was sufficient to inactive/kill the micro-organisms present in the biofilm. In the same study, also the effectiveness of caustic dosing under realistic sewer conditions was investigated during field trials. The results showed that sulfide could be effectively inhibited for 5 days.

Alkaline crown spraying is a technique that coats the exposed surface of a gravity sewer pipe with magnesium hydroxide (MgOH₂) to raise the surface to a pH of at least 9, destroying the sulfide oxidizing community [6, 53]. A drawback is that micro-organisms will slowly grow back, requiring reapplication of the caustic spray. Sydney *et al.* (1996) showed that the pH of the sewer wall was maintained at 9 for approximately 9 months after alkaline crown spraying [6]. Depending upon the rate of corrosion and the condition of the pipe, crown spraying can be a cost effective way to reduce the need for rehabilitation of the sewer and thus significantly prolong the lifetime of a sewer. So far, alkaline crown spraying has not found widespread application, mainly due to the labour intensity of this method [2].

In addition to inhibiting the SRB activity, pH elevation is also used to prevent the formation of sulfide in the molecular form (i.e. H_2S), which causes the corrosion and odour problems. The critical pH value is around pH 8 when only 10% exists as H_2S (aq) (see Figure 2.2). At pH 9, sulfide is almost entirely present as HS^- and will therefore remain in the bulk water [50, 66]. Magnesium hydroxide (MgOH_2) and sodium hydroxide (NaOH) are the chemicals most commonly used to raise the pH [2, 6, 54]. NaOH can increase the pH to 14 whereas MgOH_2 can increase the pH to a maximum pH of 9.0-9.5 as a result of the relatively low solubility of MgOH_2 [67]. The required dosing depends on the buffer capacity and the flow rate. The main disadvantage of this method is the necessity for continuous dosing, resulting in high dosing requirements and thus chemical costs.

Addition of biocides

Some studies have shown that SRB inhibition can be achieved by adding biocides such as 1,8-dihydroxyanthraquinone and other anthraquinone derivatives, gramicidin S and D, polymyxin B and molybdate [68-71]. In a study of Zhang *et al.* (2008) the addition of formaldehyde at a concentration of 12-19 mg L^{-1} was sufficient to prevent sulfide generation in sewage [72]. However, formaldehyde can be toxic and even fatal to humans at elevated concentrations [73]. Therefore, adequate protection equipment is needed for sewer workers. Until now, addition of these biocides has not found widespread application for sulfide control in sewer systems [5]. Recently, it was shown that sulfate reduction (as well as methanogenic activities) could be reduced significantly (> 90%) by the addition of nitrite during laboratory scale experiments [74]. In a study of Jiang *et al.* (2010) an intermittent nitrite dosing strategy was developed during both laboratory and field trials [75]. In this study, the effect of nitrite concentration and exposure time on the inhibition and recovery of SRB (as well as methanogens) was investigated. In a second study, the authors showed that the inhibitory effect of nitrite on sulfate reduction was caused by the biocidal effect of free nitrous acid (FNA) on SRB and methanogens [76]. Contrary to other biocides, the addition of nitrite does not come with environmental concerns as it can be easily removed by heterotrophic bacteria in sewer systems and WWTPs and may therefore become an interesting alternative for current abatement strategies [77].

2.3.1.2 Specific inhibition of SRB activity

Nitrate dosing

The effectiveness of nitrate addition to prevent the formation of hydrogen sulfide was already shown in 1949 in a study of Allen [78]. Adding nitrate enables nitrate reducing bacteria to outcompete SRB so that the production of sulfide is prevented. Podulska and Anderson (1981) found that sulfide formation could be prevented as long as enough nitrate was added to raise the redox potential above +300 mV versus standard hydrogen potential [79]. In addition to the prevention of sulfide generation, nitrate can also result in anoxic oxidation of already produced sulfide by sulfide oxidizing bacteria (SOB) [80-82]. In a study of De Lomas *et al.* (2006) it was shown that the addition of 9, 15 and 27.7 kg $\text{NH}_4\text{NO}_3 \text{ h}^{-1}$ to a 6.7 km combined sewer network in the city of Corfu with influent sulfide concentrations varying between 3 and 27 mg S L^{-1} resulted in sulfide removal efficiencies of 84%, 98% and 99%, respectively [82]. Bentzen *et al.* (1995) reported an average sulfide concentration of 0.24 mg L^{-1} in a rising main during nitrate dosing compared to average sulfide concentrations of 4.2 mg L^{-1} without nitrate dosing [80]. However, dosing of nitrate did result in a decrease in soluble BOD across the rising main. Hobson and Yang (2000) reported that the addition of nitrate to sewage entering a rising main can totally suppress the formation of hydrogen sulfide [83]. The addition of 5 mg L^{-1} nitrate at the beginning of a 61 km long gravity pipe in Tenerife (Spain) resulted in a complete inhibition of sulfide formation [84].

2.3.2 Elimination of hydrogen sulfide formed

2.3.2.1 Oxygen injection

Injection of pure oxygen is presently considered an attractive option as it is less expensive than most other chemicals and it targets rising mains where the SRB activity is the highest [85]. Oxygen inhibits the activity of SRB and oxidizes the sulfide that has been produced [32]. Sulfide can be either oxidized by means of biological sulfide oxidation by micro-organisms located in the aerobic parts of the biofilm or by chemical sulfide oxidation (as discussed in paragraph 2.1.2). The required oxygen dosage depends on the sulfide concentration, organics concentration, temperature, hydraulic retention time, oxygen demand of the biofilm, and the type and size of the sewer pipe. Several studies showed that when the dissolved oxygen concentration is 1 mg L^{-1} or higher, sulfide formation can be completely

prevented [20, 86]. Although oxygen injection is regarded as an attractive cost-effective method, it does pose some disadvantages. These include the limited oxygen solubility and the growth of heterogeneous biomass resulting in removal of readily biodegradable substrate. In addition, the storage of liquid oxygen on site is perceived to be a serious occupational health & safety (OH&S) issue. Furthermore, it is less effective in gravity sections due to the release of oxygen into the headspace of gravity sewers.

2.3.2.2 Hydrogen peroxide dosing

Hydrogen peroxide oxidizes hydrogen sulfide to elemental sulfur or sulfate, depending on the molar ratio and pH. Under typical domestic wastewater conditions the oxidation of sulfide proceeds within 15 to 60 minutes according to the following reaction [87]:



As hydrogen peroxide is a strong oxidant that reacts with most reduced compounds, the required dosage in sewers is higher than the stoichiometric requirement due to the presence of organic substances. The effective dosage rate normally varies between 1.3-4.0 times the stoichiometric requirement, whereas the obtained sulfide removal efficiencies range between 85-100% [2, 88]. Advantages of hydrogen peroxide include the harmlessness of the by-products and the fact that the breakdown of excess hydrogen peroxide will result in an increase of dissolved oxygen concentration (i.e., another SRB inhibitor). Disadvantages are the short life time in sewage and the high associated costs [56, 89]. Therefore, depending on the sewer infrastructure, it may be necessary to add hydrogen peroxide at several points in the sewer system. Due to the above-mentioned disadvantages, hydrogen peroxide is not widely used.

2.3.2.3 Chlorination

Chlorination using gaseous chlorine or aqueous sodium hypochlorite, added as aqueous solution, is one of the oldest forms of controlling sewer corrosion and odour problems. Chlorine oxidizes sulfide to either sulfate or elemental sulfur, depending on the pH [87]. At pH values lower than 7.5 colloidal sulfur is formed, whereas at higher pH values sulfate is produced [90]. The chemical oxidation reaction is slower at low concentrations, particularly below 1 mg L⁻¹ [2]. A disadvantage of chlorine dosage is that high dosing ratios are often

required as it also oxidizes organic compounds present in the sewage. Chlorine to sulfide ratios of 9-15:1 (w/w) for chlorine gas and 1.8-2.0:1 (w/w) for sodium hypochlorite, have been suggested [91]. Another disadvantage of chlorine addition is the possible formation of toxic organochloride derivatives [92], which needs to be prevented. Nowadays, due to these disadvantages, chlorine is used less and less by the water industry.

2.3.2.4 Iron dosing

Precipitation of dissolved sulfide by iron dosage is another widely used method [2, 31, 93, 94]. It is especially used in large systems as presumably other abatement strategies are less suitable for sulfide control in such sewer pipes [64]. Iron salts such as chloride, sulfate or nitrate can be added to the wastewater either in ferric or ferrous forms [95]. Ferrous iron (Fe^{2+}) removes sulfide by precipitation as ferrous sulfide, according to equation 2.16. Ferric iron (Fe^{3+}) removes sulfide by oxidizing it chemically to elemental sulfur while being reduced to ferrous iron according to equation 2.17. Subsequently, the formed ferrous iron removes sulfide by precipitation to FeS .



Because of the low solubility product (i.e. K_s of ferrous sulfide is 3.7×10^{-19}), the reaction is very effective in precipitating sulfides. Several field studies showed that despite the low solubility of iron sulfide, complete control of sulfide is difficult and therefore iron salts must be added in excess to obtain low sulfide concentrations [93, 96]. However, other studies reported that iron dosage close to or even less than its stoichiometric requirements results in complete sulfide removal [43, 97]. Furthermore, Zhang *et al.* (2009) reported a decrease in sulfate reduction rate as result of iron dosing [97]. The mechanisms behind this decline in sulfate reduction are yet to be revealed. Literature does not give a conclusive answer whether ferrous or ferric iron is most effective in removing aqueous sulfide from sewer systems [95]. Iron addition may also lead to side reactions such as the precipitation of phosphates ($FePO_4$) and complexation with ligands (e.g. Fe EDTA) [14].

2.3.3 Coating of the sewer wall

Antimicrobial surfaces are commonly used in a variety of sectors, such as medicine, dentistry and the food industry [98]. The use of antimicrobial surfaces for the prevention of biogenic corrosion is a relatively new area. Several studies were performed using different protective coatings including polyurethane and glass-fibre mat-reinforced epoxy. Redner *et al.* (1991) evaluated the effectiveness of more than 20 different protective coatings against corrosion by immersion in 10% sulfuric acid and reported varying performance after 1 year [99, 100]. Some inhibition of microbial activity was obtained when cultures of *Thiobacillus* were exposed to concrete with calcium formate added to the mixture [49]. Rivera-Garza *et al.* (2000) reported on the antibacterial effect of zeolites supporting bactericidal metal ions, such as silver and copper [101]. Recently, the effectiveness of two types of antimicrobial concrete, based on polymer fibres or metal zeolites were investigated using accelerated microbiological and chemical simulation tests [102]. The authors found the best protective performance was obtained using an epoxy coating, whereas silicates or antimicrobial compounds failed to give an improved performance under the given test conditions.

Liu and Vipulanandan (2001) reported that coating concrete with a glass-fibre mat-reinforced epoxy immersed in 3% sulfuric acid increased its lifetime 70 times [103]. The authors also reported the successful application of two different polyurethane-coated concrete when immersed in 3% sulfuric acid [104].

Although the above mentioned studies showed that these protective and antimicrobial coatings for concrete can be a successful tool against sewer corrosion, they have not found widespread application due to their (relatively) high costs. Moreover, as it does not prevent the formation of sulfide in the sewer, high sulfide concentrations can be found at the sewer outlet.

2.4 Electrochemical wastewater treatment

2.4.1 Background

The first time electricity was suggested as a means to treat wastewater dates back as far as the end of the 19th century [105]. Examples of electrochemical technologies for wastewater treatment are for example electrocoagulation, electroflotation, electrodeposition and electrooxidation. Electrocoagulation involves the in-situ production of coagulants by the use of sacrificial anodes such as aluminium and iron. In electroflotation, gas bubbles generated

during the electrolysis of water, are used to separate e.g., solids, oil and grease from the wastewater. Electrodeposition involves the recovery of metals from wastewater by deposition on the cathode electrode. Electrooxidation is used for the oxidation of pollutants by direct oxidation or indirectly by in-situ generated oxidants (see section 2.4.5).

The first large scale application of electrocoagulation in drinking water was implemented in the United states in 1946. However, applications for electrochemical technologies were limited, mainly due to expensive electricity supply and large investments costs. Over the last two decades, there has been an upsurge in interest in electrochemical technologies due to (i) reduction in the relative cost of electricity and (ii) the rapid expansion of new electrode materials. Furthermore, more stringent environmental regulations with respect to wastewater discharge have stimulated greater interest in new more efficient techniques. As a result, electrochemical technologies have become promising techniques (again) for treating wastewater.

Currently, full-scale electrochemical systems are implemented for the treatment of several industrial wastewater streams, but for example also for the production of chlorine and caustic in the chlor-alkali industry [105]. Electrochemical recovery of metals is widely applied in the metal industry, particularly from high concentration industrial process streams (e.g. effluents from the electroplating baths). Electrocoagulation has been implemented for the removal of suspended solids, oil and greases from waste streams from e.g., the textile and petroleum industry [106]. There are also several full-scale treatment facilities using electroflotation for the treatment of wastewater originating from the dairy, food processing, mining and petroleum industry [105].

2.4.2 Fundamentals of electrochemistry

2.4.2.1. Working principle of an electrochemical system

An electrochemical reactor typically consists of an anode and cathode submerged in an electrolyte solution, either in an undivided system (single chamber configuration) or in a divided system (2-chamber configuration). In 2-chambered electrochemical cells for wastewater applications, the anode and cathode compartments are normally separated by a cation exchange membrane (CEM). In the anode, an oxidation reaction occurs in which electrons are generated, while in the cathode a reduction reaction takes place in which electrons are consumed. The anode and cathode are connected through an electrical circuit.

While current flows through the electrical circuit, cations migrate through the cation exchange membrane from the anode to the cathode to maintain electroneutrality of the system. An electrochemical system can be operated by either controlling the cell voltage or the current. In Figure 2.5 a schematic overview of a simplified configuration of a 2-chambered system is presented. At the anode, sulfide is oxidized to sulfur at the electrode surface, while at the cathode oxygen is being reduced to water. However, this Figure is a simplification as in a real situation the concept is more complex as several direct and indirect oxidation processes (i.e. secondary reactions resulting from, for example, oxygen evolution and organics oxidation) in the anode chamber may occur simultaneously with several final products of oxidation (e.g. sulfur, thiosulfate and sulfate). The specific reactions that will take place and the overall process performance in terms of removal efficiency and energy requirements depend on several parameters such as the electrode material used and operational conditions applied.

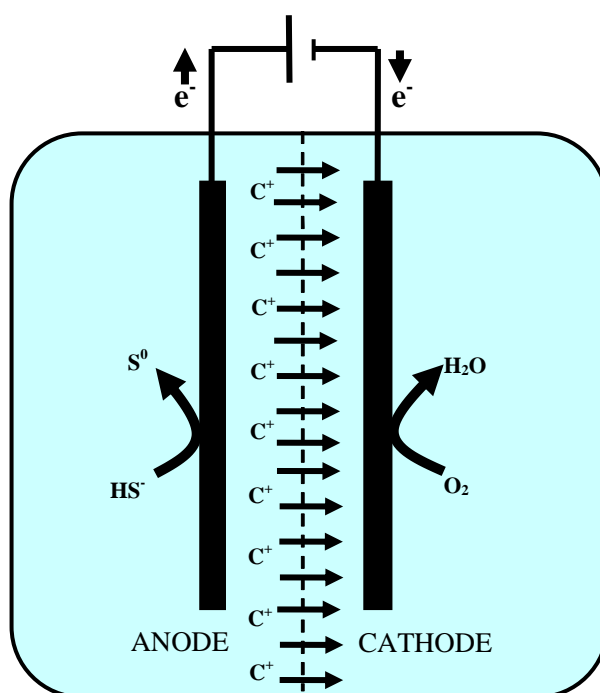


Figure 2.5 Schematic overview of a simplified electrochemical system for sulfide oxidation.

2.4.2.2 Thermodynamics of electrochemical systems

The energy change for a reaction in an electrochemical cell can be described by the change in Gibbs free energy for each half cell:

$$\Delta G = (\sum_i s_i \mu_i)_{anode} - (\sum_i s_i \mu_i)_{cathode} \quad (\text{Eq. 2.18})$$

Where ΔG is the Gibbs free energy expressed in Joule (J), μ_i the chemical potential of species i , and s_i the stoichiometric coefficient of species i . The Gibbs free energy (J) is a measure of the maximum work that can be obtained from a certain reaction. When the Gibbs free energy is negative ($\Delta G < 0$), the process is spontaneous and electricity is produced (e.g. fuel cell). On the other hand, when the Gibbs free energy is positive, energy is required (e.g. electrolysis cell). The total work performed by an electrochemical cell is related to the voltage (Volt) and the Gibbs free energy according to Equation 2.19 [107]:

$$W = E_{emf} \times Q = E_{emf} \times nF = -\Delta G \quad (\text{Eq. 2.19})$$

Where Q is the total charge transferred in Coulomb (C), F the Faraday constant (96485.3 C mol⁻¹) which is a measure for the charge per mole of electrons, n the amount of electrons involved in the reaction and E_{emf} the cell electromotive force (i.e. $E_{cathode} - E_{anode}$). If all reactions occur under standard conditions (i.e. 298.15 K and ambient pressure) it can be expressed as:

$$\Delta G^0 = -nF(E_{cathode}^0 - E_{anode}^0) \quad (\text{Eq. 2.20})$$

Where ΔG^0 is the standard Gibbs free energy and E^0 the standard potential. The Gibbs free energy of a reaction under specific conditions can be derived from the standard Gibbs free energy as follows:

$$\Delta G = \Delta G^0 + RT \ln(\Pi) \quad (\text{Eq. 2.21})$$

Where R is the universal gas constant (8.3144 J mol⁻¹ K⁻¹), T the absolute temperature (K) and Π a measure of the activities (dimensionless) of the products divided by the reactants. For the reaction $s_A A + s_B B \rightarrow s_C C + s_D D$ Π should be expressed as:

$$\Pi = \frac{a_C^{s_C} + a_D^{s_D}}{a_A^{s_A} + a_B^{s_B}} \quad (\text{Eq. 2.22})$$

In dilute systems, the activities of the products and reactant can be estimated by their concentrations:

$$\Pi = \frac{[C]^{s_c} + [D]^{s_D}}{[A]^{s_A} + [B]^{s_B}}, \text{ which equals } \Pi = \frac{[red]}{[ox]} \quad (\text{Eq. 2.23})$$

By combining equation 2.20, 2.21 and 2.23, the Gibbs free energy can be expressed in terms of potential, which is known as the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{[red]}{[ox]} \quad (\text{Eq. 2.24})$$

Where [red] is the concentration of the species of the product or reduced side and [ox] the concentration of the reactant or oxidized species. In Table 2.5 the standard electrode potentials (i.e. 298K, 1 atm, 1M) for the most important sulfur and other chemical half cell reactions that are relevant to this thesis are presented. The table shows that theoretically it should be possible to selectively oxidize sulfide before oxidation of water to oxygen or chloride to chlorine takes place.

Table 2.5. Standard electrode potentials (E^0) at pH= 7 for several sulfur and other chemical half cell reactions

Redox reaction	E^0 (V) (at pH=7)
Eq. 1. $S(s) + 2e^- + 2H^+ \leftrightarrow H_2S(aq)$	-0.270
Eq. 2. $S(s) + 2e^- + H^+ \leftrightarrow HS^-$	-0.476
Eq. 3. $S_2O_3^{2-} + 8e^- + 8H^+ \leftrightarrow 2HS^- + 3H_2O$	-0.213
Eq. 4. $SO_4^{2-} + 8e^- + 9H^+ \leftrightarrow HS^- + 4H_2O$	-0.213
Eq. 5. $SO_4^{2-} + 8e^- + 10H^+ \leftrightarrow H_2S(aq) + 4H_2O$	-0.214
Eq. 6. $SO_4^{2-} + 6e^- + 8H^+ \leftrightarrow S^0 + 4H_2O$	-0.194
Eq. 7. $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	0.817
Eq. 8. $Cl_2(aq) + 2e^- \leftrightarrow 2Cl^-$	0.945
Eq. 9. $OH^\bullet + H^+ + e^- \leftrightarrow H_2O$	1.967

a) The redox reactions presented in the Table are written as reduction potentials (although the reverse reaction occurs), according to the International Union of Pure and Applied Chemistry convention.

2.4.2.3 Electrode kinetics

Before an electrochemical reaction takes place at the interface between the electrode surface and electrolyte, the charge must overcome an activation energy barrier. This is often called the activation overpotential. The kinetics of an electrode reaction mainly depend on the activation overpotential, but also on the electrolyte composition at the electrode interface and the temperature as described by the Butler–Volmer equation [108, 109]:

$$i = i_0 \left\{ \exp \left[\frac{(1-\alpha)F}{RT} \times (E - E_{eq}) \right] - \exp \left[-\frac{\alpha F}{RT} \times (E - E_{eq}) \right] \right\} \quad (\text{Eq. 2.25})$$

where i_0 is the exchange current density (A m^{-2}), α the charge transfer coefficient (dimensionless), F the Faraday constant ($96,485 \text{ C mol}^{-1}$), E the electrode potential (V) and E_{eq} the equilibrium anode potential (V), respectively. The exchange current density measures the catalytic activity of an electrode in which a high i_0 represents a high catalytic activity towards a certain reaction. The difference between E and E_{eq} gives the overpotential of the electrode. α is the charge transfer coefficient and varies between 0 to 1.0, depending on the reaction and the electrode material [107, 110]. Therefore, the obtained current is determined mainly by the exchange density and not by α . For single step reactions involving 1 electron, instead of α , the symmetry factor β is sometimes used. The β describes the intrinsic characteristic of the given charge-transfer reaction at the given interface [110, 111]. With increasing temperatures, the exponential term of equation 2.25 decreases. However, this is offset by the increase of i_0 , with the result that higher currents are obtained. It should be noted that the Butler-Volmer equation is only valid in situations where the electrode reaction is controlled by the electrical charge transfer at the electrode surface and not restricted by mass transfer limitations. At higher current densities, the equation can be approximated as a linear relationship, and thus simplified to the Tafel equation [107]:

$$E - E_0 = a \log \left(\frac{i}{i_0} \right) \quad \text{with} \quad a = \frac{RT}{2\alpha F} \quad (\text{Eq. 2.26})$$

The above equation can be used to calculate the overpotential of electrode materials at different current densities, which is an important parameter in electrochemical conversion reactions.

2.4.2.4 Potential losses in an electrochemical system

The cell voltage is equal to the theoretical potentials plus the sum of all the losses of the system. These losses can be divided into (i) activation losses, (ii) ohmic losses and (iii) mass transfer or concentration losses [110] and can be described as follows:

$$E_{cell} = ([E_{anode} - E_{cathode}]_{theoretical}) - \eta_A - \eta_C - IR_{\Omega} \quad (\text{Eq. 2.27})$$

in which η_A and η_C are the anode and cathode overpotential (i.e. activation losses and losses due to mass transfer limitations) and IR_{Ω} the ohmic resistance of the system. Activation losses are determined by the electrode kinetics (as discussed above). Ohmic losses are determined by the resistance of the electrons through the electrodes and ions through the electrolyte as well as the membrane. Theoretically, it also includes the resistance of the electrode, however, as normally (highly) conductive materials are used this loss is often negligible. Especially in low conductive media (e.g. domestic wastewater), the ohmic losses can have a significant impact on the required cell voltage. The ohmic losses can be reduced by (i) minimizing the anode and cathode spacing, (ii) using low resistivity membranes and (iii) addition of salts to increase the electrolyte conductivity. Mass transport limitations of species towards (and away) from the electrode result in an increase in cell voltage and are normally only observed at high current densities. The mass transfer depends on the concentration of the species and the hydrodynamic flow (i.e. laminar or turbulent conditions).

2.4.3 Ion exchange membranes

In general, four types of ion exchange membranes (IEM) can be used in an electrochemical cell: (i) cation exchange membranes (CEM), (ii) anion exchange membranes (AEM), bipolar membranes (BPM), and (iv) charge mosaic membranes (CMM) [112]. The desired properties of a IEM are (i) high perm selectivity, (ii) low electrical resistance ($\Omega \text{ cm}^{-2}$), (iii) good mechanical stability, (iv) high chemical stability (i.e. resistant to low and high pH values and oxidizing agents) and (v) fabricated at low production costs [113]. A high perm selectivity means that the membrane is highly permeable to counter ions but highly impermeable to co-

ions. A good mechanical stability means that swelling or shrinking of the membrane when changing from dilute to concentrated solutions is minimal. There are several parameters influencing the above mentioned membrane properties including the degree of cross-linking, the intensity of ionic charging and the type of functional group (e.g. sulfonic or carboxylic). Often these parameters have opposing effects. For example, a higher cross-linking gives better mechanical strength but results in a higher electrical resistance as well. More ionic charge gives a low electrical resistance but often comes with a poor mechanical stability (i.e. high decrease of swelling). Hence, an optimum in composition of the different parameters needs to be found in order to develop a good ion exchange membrane. An elaborate overview of the state of the art in ion exchange membranes is presented by Nagarale *et al.* (2006, 2010) [113, 114].

In the context of electrochemical sulfide abatement in sewers, the anode and cathode needs to be separated by a CEM. Two commonly used CEM are Nafion (Dupont Co, USA) and Ultrex (Membranes International Inc., USA). The good mechanical and chemical stability of the membrane is of special concern as the membrane is exposed to a low conductive solution in the anode (i.e. domestic wastewater) and a highly conductive high pH solution at the cathode. Therefore, in this study Ultrex membranes were used as they are considered to have a good mechanical and chemical stability and low resistivity, whereas they are also more cost effective than Nafion membranes [115].

2.4.4. Electrode material

One of the most important features of an electrochemical system is the electrode material used. Ideally, an electrode material is (i) stable under the conditions applied, (ii) highly conductive, (iii) produced at low costs and (iv) possesses a high catalytic activity towards the desired reaction. Most research has been focussed on suitable anode materials as most electrochemical processes for wastewater treatment involve the anodic oxidation of pollutants [116]. An overview of anode materials commonly used for electrochemical wastewater remediation and their overpotential for oxygen evolution is presented in Table 2.6.

Table 2.6. On-set potential for oxygen evolution at commonly used anode materials versus SHE (adapted from [105])

Anode material	Standard potential for O ₂ evolution (E ⁰)
Ti/Pt	1.3
Ti/IrO ₂	1.6

Ti/Ru/Ir	1.6
Graphite	1.7
Ti/PbO ₂	1.9
Ti/SnO ₂	1.9
Ebonex (titanium oxides)	2.2
Si/BDD	2.3
Ti/Pb-Sn	2.5
Ti/BDD	2.7
Diachem	2.8

These electrode materials have different selectivity and catalytic activities, and may therefore produce different reaction products. In the case of direct oxidation of sulfide these include elemental sulfur, thiosulfate and sulfate. For indirect oxidation processes, these products could be oxygen, chlorine/hypochlorous acid, hydroxyl radicals and other reactive oxygen species. Therefore, the reactions that might take place in the context of electrochemical sulfide abatement in sewers are discussed in the following paragraph.

2.4.5 Electrochemical reaction mechanisms

Pollutants can be removed either by an oxidation reaction at the anode, or by a reduction reaction at the cathode. These reactions can take place directly at the electrode surface (i.e. direct oxidation/reduction) or indirectly, in which an oxidant is generated at the electrode surface and subsequently reacts with the pollutant in the bulk liquid (see Figure 2.6).

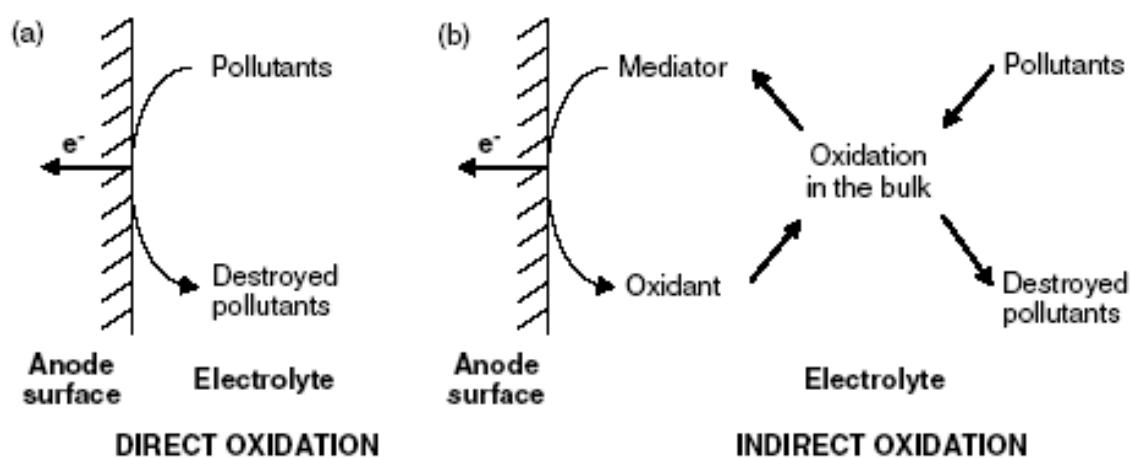


Figure 2.6 Schematic overview of direct and indirect reaction mechanisms (from [117])

Direct oxidation of a pollutant at the electrode surface can take place in case a compound is electrochemically active (e.g. sulfide) or through the generation of ‘chemisorbed and physisorbed active oxygen’ (see section 2.4.5.1). In case of indirect oxidation processes, oxidants are generated at the electrode surface and subsequently react with the pollutant in the bulk liquid. These oxidants require different potentials in order to be formed. In Table 2.7 an overview of the potential of formation of several important oxidants which can be generated electrochemically at the anode are presented.

Table 2.7 Theoretical potential of formation of several oxidants at pH=0 (adapted from [105, 118])

Oxidant	Formation potential E^0 (Volt)
H_2O/OH^\bullet (hydroxyl radical)	2.38
O_2/O_3 (ozone)	2.07
$SO_4^{2-}/S_2O_8^{2-}$ (peroxodisulfate)	2.01
MnO_2/MnO_4^{2-} (permanganate ion)	1.77
H_2O/H_2O_2 (hydrogen peroxide)	1.77
Cl^-/ClO_2^- (chlorine dioxide)	1.57
Ag^+/Ag^{2+} (silver(II) ion)	1.50
Cl^-/Cl_2 (chlorine)	1.36
$Cr^{3+}/Cr_2O_7^{2-}$ (dichromate)	1.23
H_2O/O_2 (oxygen)	1.23

Table 2.7 shows that thermodynamically, the oxidation of water to oxygen occurs at 1.23 E^0 versus standard hydrogen potential (SHE). However, in practice, higher potentials have to be applied before oxygen is being formed. The difference between the thermodynamic value and the potential at which oxygen evolution starts to take place is called the oxygen overpotential [105]. In Table 2.6 an overview of the potential of formation of oxygen (versus SHE) of commonly used electrode materials is presented. Considering the above, an electrode must possess a high enough overpotential for oxygen evolution (and low overpotential for the formation of other oxidants) in order for oxidants besides oxygen to be formed. The actual formation of an oxidant does not only depend on the electrode material used, but also on the concentration of the required mediator, the presences of other mediators, the pollutant concentration and the operational conditions applied. With respect to electrochemical sulfide abatement in sewer systems, especially the anodic formation of oxygen, reactive oxygen species (e.g. OH^\bullet radicals), chloride and the cathodic generation of hydrogen peroxide may

be of importance. In addition to these oxidants also the cathodic formation of hydroxyl ions is of importance. Therefore, these will be discussed in more detail below.

2.4.5.1 Anodic reaction mechanisms

Formation of oxygen and reactive oxygen species

According to Comninellis *et al.* (1994) reactive oxygen species such as OH^\bullet radicals are intermediate products during the oxidation of water to oxygen [119]. In Figure 2.7 a schematic overview of this mechanism is presented.

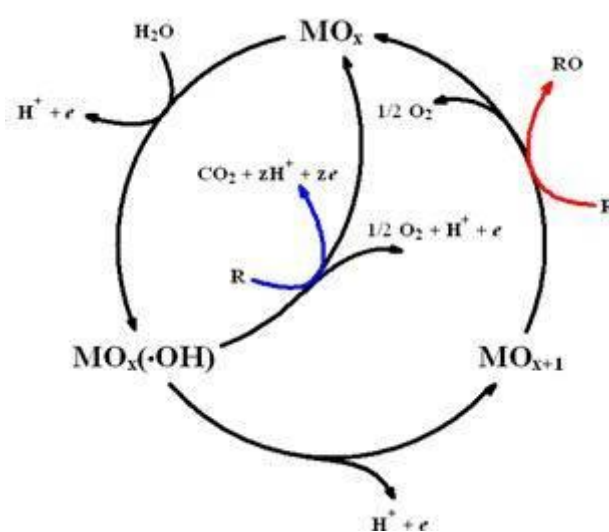


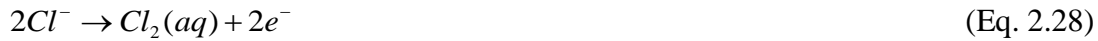
Figure 2.7. Schematic overview of the electrochemical oxidation mechanisms (from [119]).

In the first step, adsorbed OH^\bullet radicals are formed on the electrode surface. The following step depends on the electrode material used, which allows us to distinguish electrodes into two groups; ‘active’ and ‘non active’ electrodes. At the surface of ‘active’ electrodes higher oxidation states are available on the electrode surface and as a result hydroxyl radicals may interact with the anode forming the so called higher oxide, which is often called ‘chemisorbed active oxygen’. This ‘chemisorbed active oxygen’ can act as a mediator in for example the selective oxidation of organics. On the other hand, at ‘non active’ electrodes the interaction of the formed hydroxyl radicals does not take place. In this case, the formed hydroxyl radicals are often called ‘physisorbed active oxygen’. In absence of any oxidisable pollutant both ‘chemisorbed and physisorbed active oxygen’ will undergo further reaction to form oxygen. Thus, the efficiency of the formation of reactive oxygen species does not only

depend on the electrode material but also on the pollutant concentration and its reactivity towards oxidation. Hence, even at ‘non active’ electrodes oxygen evolution may become an important reaction at low pollutant concentration. The formation of oxygen is often regarded as a parasitic side reaction, as it lowers the process efficiency during for example, the oxidation of organics [120]. However, in a sewer context the formation of oxygen does not necessarily mean a decrease in process efficiency as oxygen can oxidize sulfide to sulfur, thiosulfate and sulfate as previously discussed in section 2.1.2.

Formation of chlorine

Chlorine is formed from the electrolysis of chloride according to the following reaction:



The formed chlorine can, as it diffuses away from the electrode, react with chloride or water to form trichloride or hypochlorous acid:



Hypochlorous acid is in equilibrium with hypochlorite ion (ClO^{-}) ($pK_a = 7.55$), which is known to be a more effective oxidant than hypochlorous acid. Figure 2.8 shows the speciation diagram of hypochlorous acid versus the pH. The Figure shows that under normal sewer conditions (i.e. pH 6.5-8.0) any formed chlorine would be present as a mixture of $HClO/OCl^{-}$ as it diffuses away from the electrode into the bulk liquid.

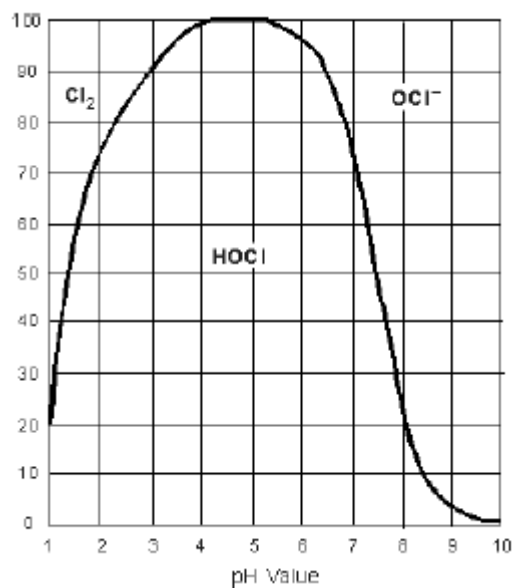


Figure 2.8 The speciation diagram of hypochlorous acid versus the pH.

Chlorine and chlorine oxygen species (i.e. ClO^- and HClO) are extensively used oxidants in industrial wastewater treatment or used as disinfection step in the production of drinking water [120, 121]. Normally, chlorine is produced by the chlor-alkali process, in which chlorine is produced from a concentrated brine solution ($30 \text{ g L}^{-1} \text{ NaCl}$) at the anode while caustic and hydrogen are being generated at the cathode. Chlorine can also be generated in-situ for wastewater remediation. Indeed, several studies showed the successful degradation of pharmaceuticals, pesticides and organics from wastewater by in-situ generated chlorine [122-124]. The lower the chloride concentrations, the more important parasitic reactions such as the oxygen evolution reaction become. Therefore, sodium chloride is sometimes dosed to increase the process efficiency, but obviously results in increasing operational costs. Chlorine can, depending on the electrode materials used, still be efficiently generated at chloride concentrations of 3 g L^{-1} [105].

In-situ chlorine generation for wastewater remediation offers several advantages compared to traditional chlorine dosage including no requirement for transport, handling and storage of concentrated chlorine/hypochloride solutions, which constitutes serious health and safety concerns and the lower energy requirements (i.e. the chlor-alkali process is a highly energy intensive process). However, as with the traditional chlorine dosage it may still result in the formation of toxic organochlorine derivatives such as chloroform and generation of toxic chlorine oxygen by-products such as ClO_2^- , ClO_3^- , ClO_4^- [123]. In addition, also brominated organic compounds can be formed. The formation of these halogenated organic compounds is

of concern in a sewer context due to the presence of a wide spectrum of different organic compounds in sewage. In coastal areas, moderate chloride concentrations up to 1 g L⁻¹ caused by seawater ingress are often observed in sewage [125]. Under these conditions, the formation of chlorine cannot be excluded.

2.4.5.3 Cathodic reaction mechanisms

The following section discusses only the formation of caustic and peroxide at the cathode, as these are considered most relevant in the context of this thesis.

Formation of hydrogen peroxide

Currently, over 95% of the world's hydrogen peroxide (H₂O₂) production is manufactured by the anthraquinone oxidation (AO) process [126]. In this process, alkyl anthraquinone is hydrogenated in the presence of Raney nickel or Palladium based catalysts. In the second step, the hydrogenated anthraquinone subsequently reacts with oxygen to form hydrogen peroxide and regenerate the alkyl anthraquinone. The hydrogen peroxide is subsequently extracted, whereas the alkyl anthraquinone is recycled to the hydrogenation step. This process can produce concentrated hydrogen peroxide solutions with concentrations up to 32 wt %. The main disadvantage of the AO process is that it is a highly energy-intensive process. Hydrogen peroxide can also be produced electrochemically by the cathodic reduction of oxygen to water:



Under alkaline conditions, hydrogen peroxide is present in the following form:



In an electrochemical system, concentrations up to 2-3 wt % can be obtained [127]. In general, the hydrogen peroxide production and its stability (i.e. hydrogen peroxide is not stable under all conditions) depends on the type of cathode used, operational conditions, anolyte and catholyte and cell configuration. Normally, carbon based materials are used as the cathode material as they are cheap whereas they possess a high overpotential for the reduction of oxygen to water [127]. The air/oxygen can either be supplied to the cathode by

sparging it into the liquid, or by diffusion using a gas diffusion electrode (GDE) [126, 128, 129]. A GDE is made of a porous PTFE material which is oxygen permeable but waterproof. An advantage of a GDE is that high oxygen partial pressures can be obtained at the electrode surfaces, where the reactions take place. In an electrochemical system, hydrogen peroxide can also be further reduced to either water (at neutral or acidic conditions) or hydroxyl ions (at alkaline conditions) according to the following reactions:



or



This results in a decrease in the coulombic efficiency (CE) of the hydrogen peroxide formation process. The formation of water is favoured under process conditions in which oxygen is the limiting factor. In addition, hydrogen peroxide can also undergo a disproportionation reaction to water and oxygen [130]:



This reaction becomes more predominant at higher hydrogen peroxide concentrations. Considering the above, several studies aimed to improve (i) the oxygen diffusion rate of GDE [131, 132], (ii) the power density and coulombic efficiency (i.e. required energy input) of the process using different carbon materials as the catalyst (e.g. carbon black, vapour grown carbon) [133] and (iii) the stability of hydrogen peroxide by the addition of H_2O_2 stabilizers (e.g., EDTA, silicate) [134].

Formation of hydroxide

In the absence of oxygen (and other reducible compounds such as organics and chlorine) the only reaction that can take place under alkaline conditions is the reduction of water to hydrogen gas and hydroxyl ions:



Thermodynamically the reduction of water under ambient pressures occurs at -0.42 Volt (E^0) versus standard hydrogen potential (SHE). In practice, lower cathodic potentials are required before this reaction takes place as electrode materials possess an overpotential for hydrogen formation. Electrode materials often used as cathode materials are nickel, titanium or stainless steel as they are relatively cheap and have a high catalytic activity (i.e. low overpotential) towards hydrogen evolution. In the presence of oxygen caustic can also be formed via the reduction of oxygen to hydroxide:



2.4.6 State of the art of electrochemical sulfide removal

A number of studies on aqueous electrochemical sulfide oxidation have been performed in the past. Most of these studies reported on the direct oxidation to elemental sulfur using high strength/conductivity solutions such as synthetic media [9, 135, 136] and brine solutions [137-141] using carbon based materials using a single chamber reactor. In these studies sulfide was present at high concentrations, whereas low current densities were applied. Other studies investigated the oxidation of sulfide using platinum electrodes [135, 142] and titanium based electrodes [143-146]. Also here, mostly single chamber reactors, high sulfide concentrations and high strength/conductivity synthetic media were used. In most of the above mentioned studies, elemental sulfur was found to be the final product of oxidation. The reason for this is that in these studies low anode potentials were applied, which is sufficient for the oxidation of sulfide to elemental sulfur (see Table 2.5). However, at higher anode potentials not only elemental sulfur but also e.g. thiosulfate and sulfate, dithionate (S_2O_6), and polysulfides can be formed. In addition, at higher anode potentials also indirect processes such as the oxygen evolution reaction can take place [143]. For example, in a study of Waterston *et al.* (2007) continuous electrochemical sulfide oxidation was achieved using boron doped diamond (BDD) at almost near-quantitative conversion to sulfate in the presence and absence of 1% NaCl [147].

A major drawback of direct oxidation to elemental sulfur is that sulfur is effectively an insulator with an electrical resistivity of approximately $10^{17} \Omega \text{ cm}^{-1}$ [148]. Indeed, electrode

passivation as result of sulfur deposition on the electrode surface has been identified as the major limitation of this process [137, 149, 150]. Thus, a technique is needed to remove the elemental sulfur from the electrode surface in order to enable practical implementation of this technology. Several strategies have been suggested to overcome anode passivation or regenerate sulfur loaded anodes including the use of (i) organic solvents [151], (ii) rotating wiper-blade electrode [152], (iii) controlled sulfur precipitation in the bulk solution with alkali addition at elevated temperatures [153], and (iv) a high voltage pulse to further oxidize the chemisorbed sulfur [154]. These methods have several disadvantages including the addition of toxic organic solvents and high energy requirements. Recently, it was shown that sulfur passivated graphite electrodes could also be depassivated by electrochemical regeneration by means of polarity switching (i.e. anode become cathode and vice versa) [155]. At the cathode, deposited elemental sulfur is reduced to sulfide and/or polysulfide. An advantage of this method is that the cathodic reduction of sulfur can be coupled to the anodic oxidation (and thus removal) of sulfide from wastewaters. Hence, sulfide is being removed from the wastewater in the anodic compartment, while the cathode (formerly the anode) is regenerated.

To date, only a few studies have been performed on the removal of sulfide from real wastewater. Some studies have been performed on the oxidation of sulfide from tannery wastewater using mixed metal coated (MMO) titanium electrodes [156, 157]. However, in these studies a single chamber electrochemical cell was used, whereas the objective was not to selectively remove sulfide, but also aimed to oxidize several components such as COD, total Kjeldahl Nitrogen (TKN), sulfide and TOC. In addition, the sulfide concentrations and conductivity of the tannery wastewater were much higher than the sulfide concentrations and conductivity observed in sewage. Recently, it was shown that sulfide could be oxidized to sulfur and recovered from paper mill anaerobic treatment effluent using a 2-chambered electrochemical cell [10]. In this study, sulfide was present at moderate concentrations (i.e. $44 \pm 7 \text{ mg L}^{-1}$ compared to $\sim 10 \text{ mg L}^{-1}$ in sewage) and oxidized at low current densities using carbon brushes and graphite granules as the anode material. The latter is not possible in a sewer context as (i) high current densities have to be applied due to the large flows (i.e. the required surface area would be too large) and (ii) the sewage needs to flow freely through the anode chamber as it contains solids and debris which would result in blockage of the system. To the author's best knowledge, until now, no studies have been reported on the (selective) removal of sulfide from domestic wastewater, let alone in sewer systems.

3. Thesis overview

As previously described in section 2.4.6 the concept of aqueous electrochemical sulfide oxidation has mainly been restricted to the selective oxidation of sulfide using high strength/conductivity solutions (synthetic feed and brine solutions) using carbon based materials at high sulfide concentrations and low current densities. Electrochemical sulfide removal from sewer systems is yet to be tested. Therefore, the overall aim of this thesis is to develop a new technology using an electrochemical cell for sulfide abatement in sewer systems by either the oxidation of sulfide and/or to avoid sulfide production. There are significant conceptual and technological challenges to be addressed to further develop the technology and to apply it to real wastewater. This chapter describes the main objectives, the research methodology and the analytical techniques used.

3.1 Thesis objectives

i. To fundamentally understand the reaction kinetics of anodic sulfide oxidation in synthetic feed and real sewage at high current densities

We aimed to selectively oxidize sulfide to elemental sulfur by direct oxidation at the electrode surface. The reason for this is threefold: (i) the oxidation of sulfide to sulfur only requires 2 electrons and thus requires the least amount of energy input, (ii) there are no side reactions that lowers the coulombic efficiency of the process (e.g. oxidation of organics), and (iii) the possible recovery of the electrodeposited sulfur, a valuable product with a market value. The removal of organics does not only result in higher energy requirements of the system, but may also have an impact on the downstream WWTP as they are needed for nutrient removal. Therefore, the first objective was to determine the relative importance of selective (i) direct sulfide oxidation to elemental sulfur and (ii) indirect sulfide oxidation in the bulk solution. Secondly, we investigated the impact of the current density applied, the presence of alternative electron donors (i.e. acetate) and chloride (i.e. at concentrations normally found in sewage) on the kinetics of sulfide oxidation using synthetic feed. In addition, trace elements in concentrations normally found in sewage, were added to investigate their catalytic effect (i.e. catalysts for auto-oxidation of sulfide with oxygen) on chemical sulfide oxidation with in-situ oxygen generation. An overall mass and charge balance was made to determine the coulombic efficiency of the process and the final products of oxidation.

ii. To determine the impact of electrode material and chloride concentration on the sulfide removal process from sewage

The results of the experiments of the first objective showed that indirect oxidation of sulfide by in-situ generated oxygen was the predominant reaction mechanism using Ta/Ir coated titanium electrodes. These electrodes are known to have a high catalytic activity towards oxygen generation. However, other types of electrodes possess different selectivity and catalytic activities, and may hence produce different intermediates. For example, oxygen, chlorine, hydroxyl radicals, ozone and other reactive oxygen species can be formed. These intermediates may have a different product spectrum for sulfide oxidation, and may increase/decrease overall oxidation efficiency. Therefore, the second objective aimed to determine the impact of 5 different types of electrocatalyst materials, namely Ta/Ir, Pt/Ir, Ru/Ir, PbO₂ and SnO₂, on anodic sulfide oxidation in sewage in terms of sulfide removal efficiency and energy requirement. In addition, we also assessed the impact of the chloride concentrations on the sulfide oxidation process. Especially in coastal areas (e.g., Queensland, Australia) elevated chloride concentrations up to 1 g L⁻¹ have been observed due to marine infiltrations into the sewer system. At these high chloride concentrations, the in-situ generation of chlorine may become an important reaction mechanism for sulfide oxidation from domestic wastewater.

iii. The development of a suitable cathode process beneficial in the context of sewer corrosion

The first two objectives of this thesis solely focussed on the anodic oxidation of sulfide. However, the electrons derived from the anode during anodic sulfide oxidation, are used at the cathode in a reduction reaction. Three reactions can be considered: (i) the reduction of oxygen to hydrogen peroxide, (ii) the reduction of oxygen to water and (iii) the reduction of water to hydroxyl ions and hydrogen. The generation of hydrogen peroxide or hydroxyl ions (i.e. caustic solution) is preferred as they both are beneficial products in the context of sewer corrosion abatement (see section 2.3.2.2 and 2.3.2.3). Therefore, the third objective of this study was to determine the feasibility of hydrogen peroxide and caustic generation. The feasibility of hydrogen peroxide generation was investigated using inexpensive carbon based gas diffusion electrodes with different catalytic layer composition and PFTE composition for the efficient cathodic generation of hydrogen peroxide.

iv. To demonstrate the long-term performance of the technology under sewer conditions during field trials.

The first two objectives showed that anodic sulfide oxidation in synthetic feed and sewage under controlled laboratory conditions is feasible. However, under realistic sewer conditions also (bio)fouling, ragging and particle settling, which was not observed during the laboratory scale experiments, may occur. In addition, the excess oxygen formed in the laboratory scale studies was transferred to the headspace whereas in a practical situation this would potentially remain in the water phase in the rising main. Hence, the objective was to demonstrate the potential of sulfide removal from domestic wastewater using an electrochemical cell by demonstrating its working principle and the long term performance under realistic sewer conditions. Several key process parameters such as the coulombic efficiency for dissolved oxidation generation and sulfide removal, the feasibility of periodic polarity switching (to overcome scaling issues) and its impact on the energy requirements were investigated. In addition, the impact of the pH (i.e. 12-14) and the polarity switching on the electrode life time was investigated during accelerated life time experiments.

v. To address the most critical engineering considerations and determine the economical and practical potential of electrochemical sulfide abatement in sewer systems

In addition to the above mentioned process parameters, also significant conceptual challenges have to be addressed in order to successfully implement this technology in full scale. Several engineering issues including prevention of particle settling and accumulation, prevention of biomass accumulation on the electrode material, precipitation of inorganics, diurnal flow variations, sufficient mixing for mass transfer, minimizing electrode losses and scaling of electrode and membrane surface have to be solved. Therefore, the objective was to design a system in which problems with blockage, ragging and scaling due to precipitation of inorganics (i.e. the most critical engineering parameters) are avoided where possible or minimized. A thorough cost analysis, based on the obtained experimental results in this thesis, was performed to thoroughly review all the results from an economic, technical and scientific perspective. In addition, a comparison with existing and emerging competitive technologies and electrochemical sulfide abatement was made in order to give a recommendation towards application.

3.2 Research methodology

In this paragraph the electrochemical cell and operation, the analytical methods and the measurements and calculation to determine the reactor performance used during the different laboratory scale studies and field trials are described. A detailed description of the experiments can be found in the appendices A-E.

3.2.1 Electrochemical cell and operation laboratory scale experiments

During the experiments conducted in this thesis, two types of 2-chambered electrochemical cells and one type of undivided cell were used (see Figure 3.1). The 2-chambered electrochemical cells were constructed using the same materials, but differed in size and shape.

Reactor A consisted of two parallel Perspex frames with internal dimensions of 14×12×2 cm. The cell was separated by a cation exchange membrane (Ultrex CM17000, Membranes International Inc., USA) creating an anode and cathode volume of 336 mL. A mesh shaped Ta/Ir MMO (IrO₂/TaO₂: 0.65/0.35) coated titanium electrode with a projected surface area of 100 cm² (Magneto Anodes BV, The Netherlands) was used as the anode material. In the cathode a stainless steel fine mesh (168 cm²) with a stainless steel current collector (6 mm mesh size, 0.8 mm wire) was used in the anodic experiments was used.

Reactor B consisted of two parallel Perspex frames with internal dimensions of 20×4.8×1.2 cm. The cell was separated by a cation exchange membrane (Ultrex CM17000, Membranes International Inc., USA) to create an anode and cathode compartment each with a volume of about 100 mL. In the anode chamber, mesh shaped Ta/Ir (TaO₂/IrO₂: 0.35/0.65), Ru/Ir (RuO₂/IrO₂: 0.70/0.30), Pt/Ir (PtO₂/IrO₂: 0.70/0.30), PbO₂ and SnO₂ coated titanium electrodes (diameter: 240 mm; thickness: 1 mm; specific surface area: 1.0 cm² cm⁻²) were used (Magneto Anodes BV, The Netherlands). The type of electrode material used depended on the study performed. At the cathode, either a stainless steel fine mesh (24 cm²) with a stainless steel current collector (6 mm mesh size, 0.8 mm wire connected via a 6 mm stainless steel rod) or a Pt/Ir (PtO₂/IrO₂: 0.70/0.30) coated titanium electrode was used as the cathode material. Both the anode and cathode had a projected electrode surface area of 24 cm².

Finally, for the accelerated electrode life time experiments, we used standard undivided electrochemical cells as described in the standard method [158]. This **Reactor C** consisted of glass beaker with a volume of 2 L. Ru/Ir (RuO₂/IrO₂: 0.70/0.30) and Pt/Ir (PtO₂/IrO₂:

0.70/0.30) coated titanium electrodes (diameter: 22.3 mm, 390 mm² electrode surface area) were used as both anode and cathode material (Magneto Anodes B.V., The Netherlands).

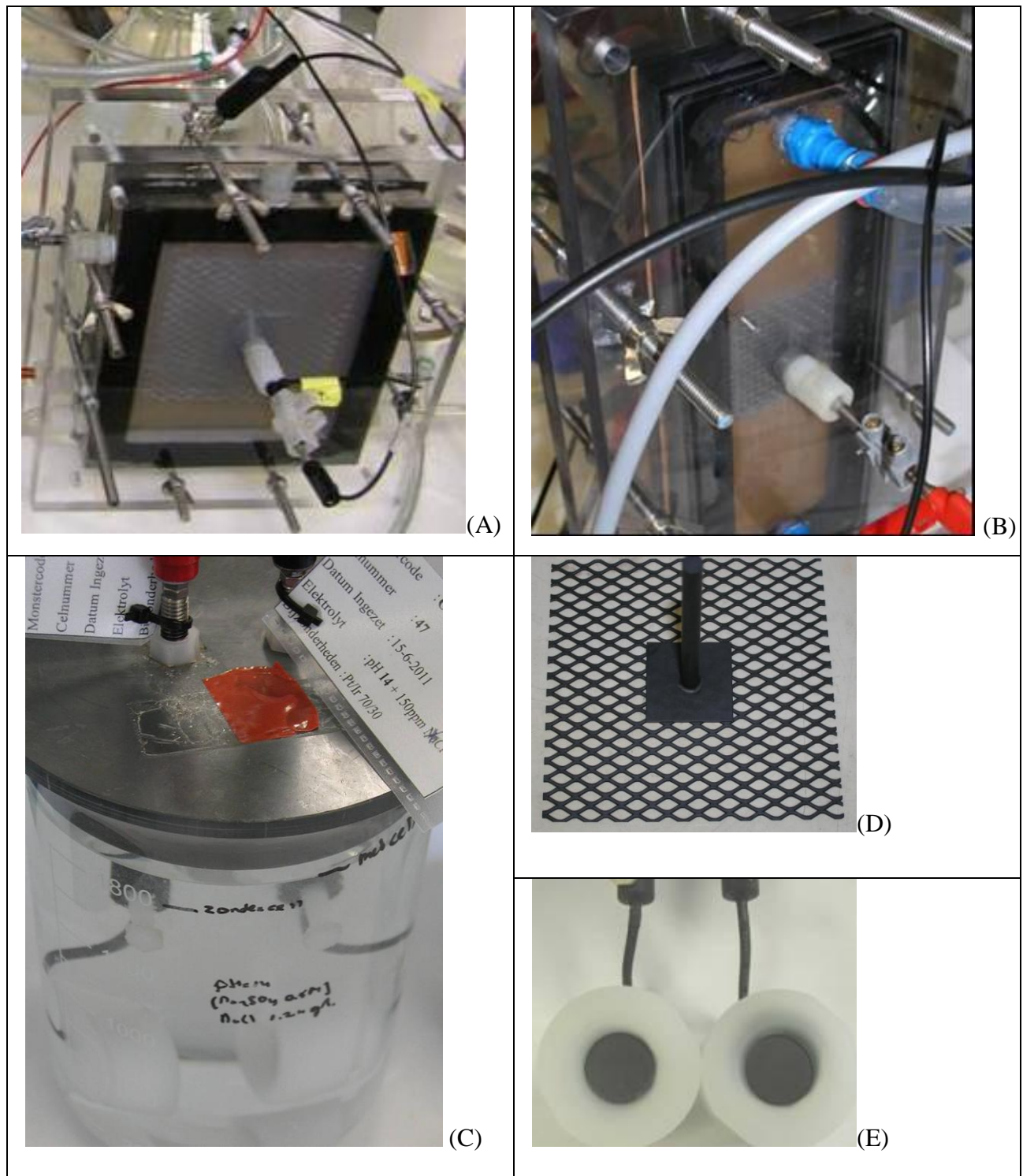


Figure 3.1. (A) Reactor used for the experiments as reported in appendix A, (B) reactor used for the experiments reported in Appendix B, C and D, (C) reactor used for accelerated life time experiments as

reported in Appendix D, (D) example of mesh shaped MMO coated titanium electrodes used in the experiments, and (E) electrodes used for the accelerated life time experiments.

In the experiments that investigated the anodic sulfide oxidation (i.e. research objective i and ii), the anode liquid medium was constantly recirculated over an external buffer vessel with a volume of 5 L. A concentrated sulfide solution was continuously added to the inlet to give an anode influent concentration of $\sim 10 \text{ mg S L}^{-1}$ by assuming that the recirculated wastewater contained no sulfide. The reason for this operation in fed batch mode was that a once through system would have required cubic metre volumes of defined media/sewage per day to enable operation of the reactors at the desired current densities. The latter was not practical in the laboratory. The disadvantage of this recirculatory mode, however, is that the “influent” sulfide concentration into the reactor will slowly increase if 100% removal efficiency is not achieved. In the experiments, the sulfide concentrations increased to 30 to $\sim 90 \text{ mg L}^{-1}$ in the experiments using reactor A, depending on the current applied and anode medium used, as the experiments progressed. Therefore, in the following studies, reactor B (i.e. smaller electrode surface area and better flow regime) was used in order to work at lower sulfide concentrations during experiments using continuous sulfide addition compared to the initial study. Here, the sulfide concentrations only increased to $\sim 5\text{-}10 \text{ mg L}^{-1}$ in all experiments.

3.2.2 Electrochemical monitoring and calculations

In all experiments, galvanostatic measurements and control were performed using a Wenking potentiostat/galvanostat (KP07, Bank Elektronik, gmbH, Germany). The anode and cathode potentials and the current were recorded every 1-5 minutes, depending on the experiment performed, using an Agilent 34970A data acquisition unit. In all experiments, an Ag/AgCl (RE-5B, Bio Analytical, USA) was used as the reference electrode. Its potential was estimated at +197 mV versus standard hydrogen electrode (SHE). The coating thickness of the electrodes (g m^{-2}) was determined by X-ray fluorescence measurement (XRF). The coulombic efficiency (ϵ) was calculated by the ratio of the amount of electrons used for the desired reaction (i.e. sulfide oxidation, dissolved oxygen generation, hydroxyl ions or hydrogen peroxide) to the total amount of electrons transferred from the anode to the cathode. For an electrochemical cell running in batch mode, the total Coulombs was determined by:

$$\varepsilon = \frac{FnV_{anode}\Delta S}{M \int_0^{t_{end}} Idt} \quad (\text{Eq. 3.1})$$

Where M is the molecular weight (g mol^{-1}), F is Faraday's constant ($96,485 \text{ C mol}^{-1}$), n is the moles of electrons exchanged per mole of compound oxidized/reduced, V_{an} is the volume of liquid in the anode compartment (m^3), and ΔS is the amount of a compound removed or generated over the course of the experiment (g m^{-3}). For an electrochemical cell running in continuous mode, the coulombic efficiency was calculated on the basis of current generation under steady state condition:

$$\varepsilon = \frac{Fnq_{anode}\Delta[C]}{MI} \quad (\text{Eq. 3.2})$$

Where q is the volumetric influent flow rate and $\Delta[C]$ is the difference in the influent and effluent compound concentration.

3.2.3 Chemical analyses

Sulfide, sulfite, thiosulfate, sulfate and chloride concentrations were measured with Ion Chromatography (IC), using the Dionex 2010i system, according to Keller-Lehman *et al.* (2006) [159]. Samples collected from the reactors were immediately filtered by a $0.22\mu\text{m}$ syringe filter (Millipore, USA) and preserved in previously prepared sulfide antioxidant buffer (SAOB) solution prior to ion chromatography analysis. SAOB solution was also used to dilute the samples when necessary. SAOB solution was prepared using nitrogen purged MilliQ ($18 \text{ M}\Omega$) water, 3.2 g L^{-1} NaOH and 2.8 g L^{-1} α -ascorbic acid. After preparation, the solution was kept refrigerated, shielded from light and not used beyond 24 hours. Sulfide concentrations were also measured with a handheld ion selective electrode for sulfide measurements (Sentek, Sentek Type 3225, United Kingdom).

The pH, conductivity and temperature were measured by using a handheld conductivity meter (Cyberscan PC 300, Eutech Instruments). The pH of the cathode compartment was determined by alkalinity titration using a 1 M hydrochloric acid solution during the caustic generation experiments. COD concentrations were determined by means of COD cuvette tests (Merck, range $25\text{-}1500 \text{ mg L}^{-1}$). Volatile fatty acids (VFAs) concentration was determined by High Performance Liquid Chromatography (HPLC). Prior to analysis, 0.9 mL of sample was filtered into 0.1 mL of 10% formic acid. The ammonium concentrations were

analysed using a Lachat QuikChem8000 (Lachat Instruments, USA) flow injection analyser (FIA). Other cations (e.g. Sodium, Potassium, and Calcium) were measured with inductively coupled plasma optical emission spectrometry (Perkin Elmer ICP-OES Optima 7300DV, Perkin Elmer, USA). The produced gas was collected in gas collection bags (SKC Tedlar 1 Litre Sample Bag) and subsequently analysed for O₂ concentrations using a gas chromatograph (Shimadzu, molecular sieve, stainless steel, 6 ft × 1 × 8" OD).

4. Research outcomes

This chapter describes the main research outcomes of this thesis and is divided into four paragraphs. Paragraph 4.1 describes the reaction kinetics of anodic sulfide oxidation in synthetic feed and sewage at high current densities using Ta/Ir electrodes. In paragraph 4.2, the impact of electrode material and chloride concentration on the anodic oxidation from sewage is discussed. Then, results of electrochemical caustic generation from sewage are described in paragraph 4.3. Finally, the long-term performance of electrochemical sulfide removal under real sewer conditions during field trials is discussed in paragraph 4.4.

4.1 Reaction kinetics of anodic sulfide oxidation in synthetic feed and real sewage at high current densities using Ta/IrOx electrodes

We aimed to selectively oxidize sulfide to elemental sulfur at the electrode surface as (i) this reaction only involves 2 electrons and (ii) any side reactions that lower the CE such as organics oxidation are avoided. For a practical application in sewers, a high current density is required as a low current density would require a too large reactor size, which is not feasible. We therefore investigated the anodic sulfide oxidation at high current densities. The results indicated that the limiting current density for direct sulfide oxidation was very low (i.e. $< 0.1 \text{ mA cm}^{-2}$) due to diffusional limitations at the low sulfide concentrations typically found in sewage. Thus, at the applied current densities in this study (i.e. $2.5\text{-}10 \text{ mA cm}^{-2}$) removal of sulfide was predominantly achieved by indirect oxidation in the bulk liquid.

In all experiments, a mixture of elemental sulfur, thiosulfate and sulfate was obtained as the final products of oxidation. Increasing the current density from 5.0 to 10 mA cm^{-2} (at the same sulfide dosing rate) did not result to a proportional increase in sulfide oxidation, thus decreasing the coulombic efficiency of the process. However, it did result in an increase in gas production, indicating that more oxygen was formed. Indeed, analysis of the produced gas showed that excess oxygen was produced. In addition, the obtained sulfide removal rate in the experiments using sewage were similar to the sulfide oxidation rate from sewage with pure oxygen addition [160] (i.e. 23.5 ± 3.0 versus $28.7 \text{ mg S L}^{-1} \text{ h}^{-1}$ at a sulfide concentration of 30 mg L^{-1}). Hence, this suggests that sulfide oxidation by means of in-situ generated oxygen was significant. To further support this hypothesis, experiments using trace elements were performed as they are known to increase the kinetics of chemical sulfide oxidation with oxygen [161]. The results showed that the sulfide removal rate increased with $37 \pm 18 \%$ in the

presence of trace elements, which is a further indication for sulfide oxidation by in-situ generated oxygen being the predominant reaction mechanism.

Normally, a considerable amount of the organics in sewage is present in the form of acetate. Acetate plays an important role in the biological nutrient removal process in downstream WWTPs. In addition, the presence of chloride in the sewage might result in the formation of chlorine, which can react with sulfide and affect the kinetics of sulfide oxidation. The results showed that both the acetate ($424 \pm 8 \text{ mg L}^{-1}$) and chloride ($170 \pm 5 \text{ mg L}^{-1}$) concentrations remained constant over the course of the experiments, whereas neither an increase nor a decrease in the sulfide oxidation rate was observed.

In all experiments, the anode liquid medium was constantly recirculated and as a result the sulfide concentration in the reactor increased to 30 to $\sim 90 \text{ mg L}^{-1}$, depending on the current applied and anode medium used, as the experiments progressed (see Appendix A for a detailed description of the experimental setup). As the sulfide concentrations in sewers normally are around 10 mg L^{-1} , batch test were performed to investigate if sulfide could also be removed at these low concentrations (see Figure 4.1). These batch tests showed that sulfide was removed to a concentration below 2 mg L^{-1} at an oxidation rate of $3.4 \pm 1.0 \text{ mg S L}^{-1} \text{ wastewater h}^{-1}$. This is in agreement with values found in literature ($1.5\text{-}5.2 \text{ mg S L}^{-1} \text{ h}^{-1}$) for chemical sulfide oxidation with oxygen in domestic wastewater at low concentrations [19, 32, 162].

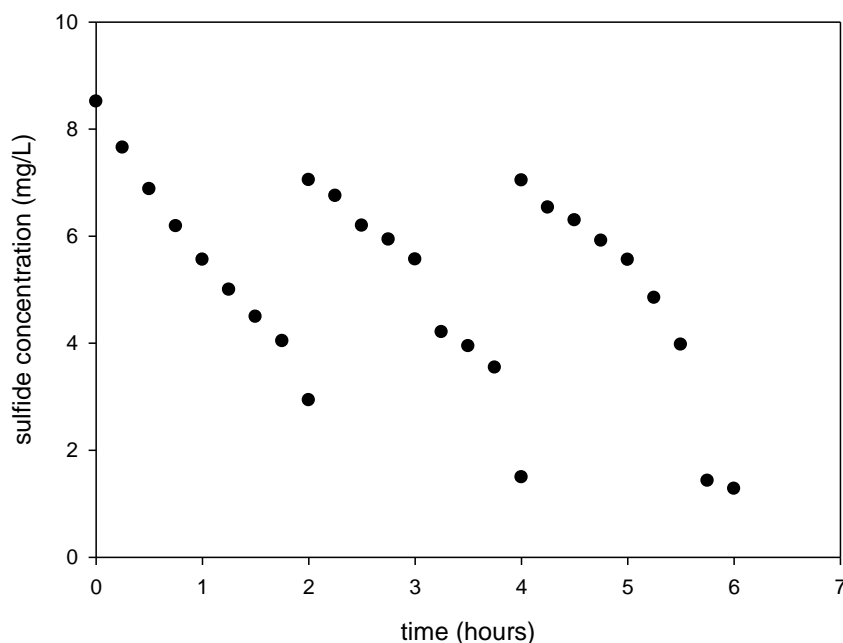


Figure 4.1. Sulfide concentration (mg L^{-1}) profile using at a current density of 5.0 mA cm^{-2} using domestic wastewater spiked with sulfide.

4.2 Impact of electrode material and chloride concentration on the kinetics of sulfide oxidation from domestic wastewater

In a second phase, the influence of the electrode material on the kinetics of anodic sulfide oxidation was investigated during 6-hour experiments at a fixed current density of 10 mA cm^{-2} using Ta/Ir, Pt/Ir, Ru/Ir, PbO_2 and SnO_2 coated titanium electrodes (see Appendix B for a detailed description of the experimental procedures). The coulombic efficiency was calculated based on the oxidation of sulfide to sulfate as (i) the results of the first objective showed that a mixture of sulfur species was formed and (ii) if oxidants other than oxygen are formed we would expect the oxidation of sulfide to sulfate. The obtained removal and coulombic efficiencies at a sulfide concentration of $\sim 10 \text{ mg L}^{-1}$ using Ta/Ir, Ru/Ir, Pt/Ir, PbO_2 and SnO_2 were equal to 78 ± 5 , 77 ± 1 , 85 ± 4 , 83 ± 2 and $84 \pm 1\%$, respectively. This is equal to sulfide removal rates of 7.5 ± 0.3 , 7.7 ± 0.5 , 7.7 ± 0.2 , 7.8 ± 0.7 and $7.8 \pm 0.6 \text{ mg S L}^{-1} \text{ h}^{-1}$, which are in agreement with the chemical sulfide oxidation rates found under high dissolved oxygen concentrations in domestic wastewater at a sulfide concentration of $\sim 10 \text{ mg L}^{-1}$ [160].

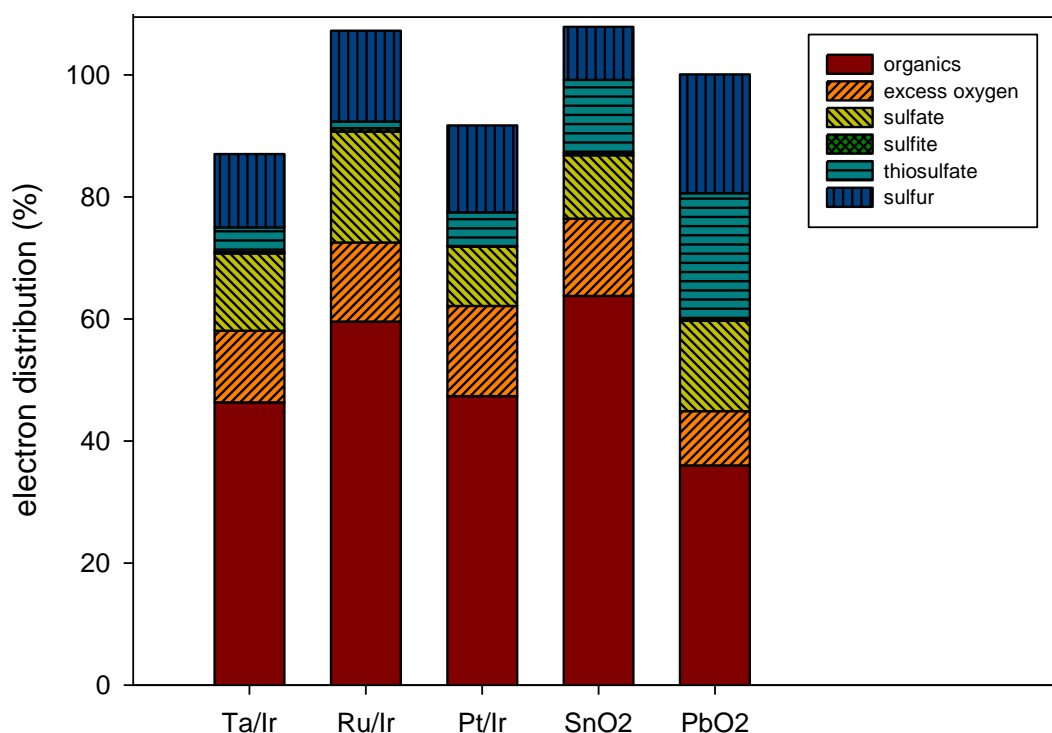


Figure 4.2. Electron distribution (%) among the different electron sinks (i.e. sulfur, thiosulfate, sulfite, sulfate, excess oxygen and organics) during the oxidation of sulfide using Ta/Ir, Ru/Ir, Pt/Ir, PbO_2 and SnO_2 electrodes at a current density of 10 mA cm^{-2} ($n=1$).

In addition, if reactive oxygen species were primarily responsible for sulfide oxidation, we would have expected sulfate to be the primary product of oxidation, contrarily to the results (see Figure 4.2). Thus, the results suggest that the kinetics of sulfide removal by in-situ generated oxygen was significant and not affected by the electrode material, even though PbO_2 and SnO_2 are known to have high catalytic activities towards reactive oxygen species generation. The latter can be explained as follows: reactive oxygen species such as OH^\bullet radicals are intermediate products during the oxygen evolution reaction. During the first step in this reaction reactive oxygen species are formed on the electrode surface. In absence of any oxidisable pollutant this 'active oxygen' subsequently converts to oxygen. Considering the relatively low pollutant concentration in sewage, high coulombic efficiencies for oxygen evolution can be obtained.

The results of the experiments at elevated chloride concentrations, often observed in coastal areas, showed that chloride concentrations of up to $\sim 1100 \text{ mg L}^{-1}$ did not entail any significant difference in sulfide removal rate. In addition, a similar electron distribution among the different electron sinks was obtained as with typical sewage chloride concentration ($\sim 100\text{-}150 \text{ mg L}^{-1}$). Analysis revealed that no free chlorine or other reactive oxygen species (which are also detected with the used method) were present even at high chloride concentrations. However, it cannot be excluded that chlorine was formed and instantly reacted with the sulfide and/or organics present.

4.3 Electrochemical caustic generation from sewage

Prior to the project we hypothesised that both hydrogen peroxide and caustic soda were interesting products that could be product cathodically, while oxidizing sewage anodically. However, preliminary results (experimental methodology and data are shown in Appendix E) showed that a long term stable operation for the cathodic generation of hydrogen peroxide could not be achieved, which was most likely caused by blockage of the GDE by NaOOH or $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$. Therefore, we have focused our attention on the cathodic production of caustic.

We postulated that it should be feasible to generate a concentrated caustic solution from sewage in the cathode chamber without significant pH changes in the anode chamber (i.e. sewage based). This can be achieved if the cathode is operated in batch or limited flow mode in which only a small volume of catholyte is recirculated (i.e. long HRT, i.e. days) while the anode (sewer based) is operated in a continuous mode (i.e. very short HRT, i.e. minutes). When a sufficient amount of caustic is produced it can be dosed to the sewer. As caustic is

only periodically dosed to the sewer to create a peak pH for a short period (e.g. 2 hours) to deactivate the sewer biofilm (see section 2.3.1.1) a much smaller reactor size is required than the case where full anodic oxidation of sulfide at the anode is the objective.

The direct generation of caustic from sewage was experimentally demonstrated during 4-hour experiments, in which the direct production of caustic from sewage at a current density of 10 mA cm^{-2} using Pt/Ir coated titanium electrodes was investigated. The results showed that a concentrated caustic solution, at a concentration of $0.61 \pm 0.1 \text{ wt } \%$ could be generated from sewage at an average coulombic efficiency of $53 \pm 8\%$ ($n=10$). It was found that the decrease in coulombic efficiency was caused by the transport of protons from the anode to the cathode and back-diffusion of hydroxyl ions from the cathode to the anode, with both processes being of similar importance. In the anode, protons are constantly generated during the oxidation reaction. Therefore, at the current density applied, a high proton concentration in the close vicinity of the anode surface can be expected. This caused a significant migrational transport of protons to the cathode as discussed above. Therefore, we investigated if the use of spacers to increase the distance between the anode and membrane surface, could lead to a reduction in proton cross-over. The obtained caustic recovery using spacers was $46 \pm 7\%$ ($n=3$). Hence, the use of spacers did not result in a reduction in proton cross-over. However, they did result in an increase in energy requirements of the system.

During the course of the experiments the anode and cathode potentials remained constant, whereas the overall cell potentials increased, as shown in Figure 4.3.

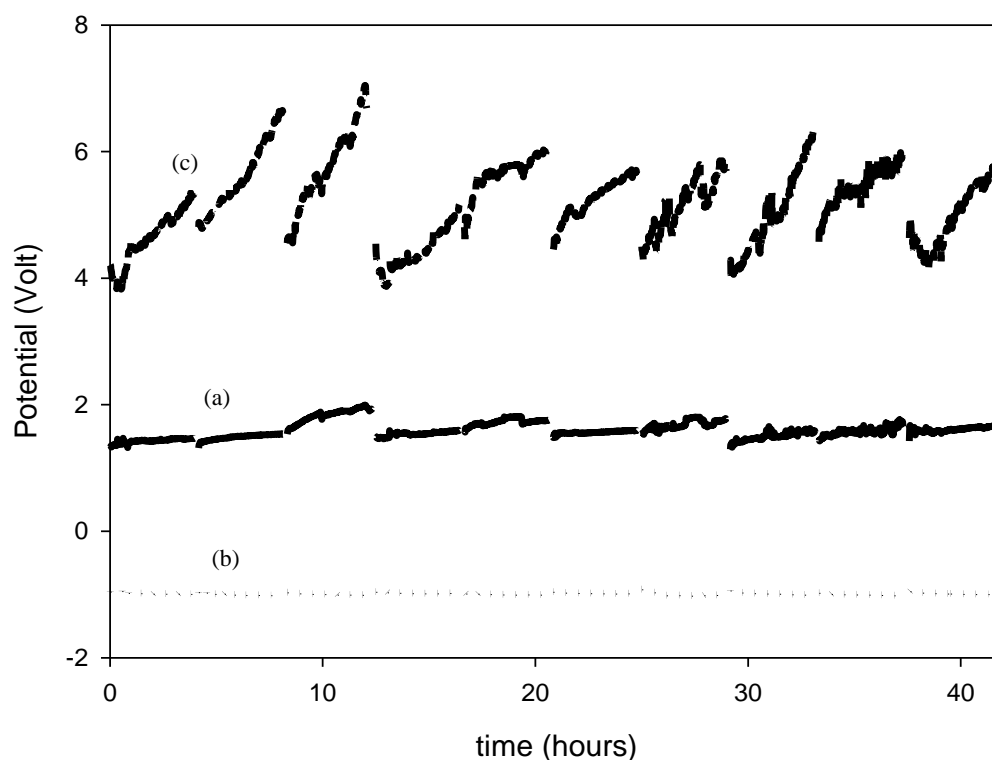


Figure 4.3. Typical profile of the (a) anode potential, (b) cathode potential and (c) cell voltage during caustic generation from sewage using Pt/Ir electrodes at a current density of 10 mA cm^{-2} without spacers ($n=10$). Every four hours the polarity of the cell was switched (i.e. anode became cathode and vice versa).

Since the anode and cathode potentials remained constant the increase in the overall cell voltage was most likely caused by an increase in membrane resistance. This is a result of the transport of bivalent cations like calcium to the cathode, which in turn causes blockage of the membrane surface by precipitation of inorganics (due to the high pH). This hypothesis was supported by ICP analysis which showed the presence of calcium, magnesium and potassium in the cathode chamber. In addition, scaling was visually observed on the membrane surface by the end of each cycle. Analysis of the precipitates on the membrane and electrode surface at the end of the field trials confirmed the presence of calcium and magnesium (see section 4.4). To overcome these scaling issues, chemical cleaning with acid or polarity switching (i.e. anode becomes cathode and vice versa) can be considered. Due to the generation of protons during the oxidation reaction, locally high proton concentrations and thus low pH values in the vicinity of the membrane surface can be expected. Hence, it should be feasible to dissolve the scaling on the membrane surface by switching the polarity. Indeed, Figure 4.3 shows that after switching the polarity every four hours, the cell voltage returned to its original value.

4.4 Long term performance of sulfide removal from domestic wastewater during field trials

Field trials were performed to demonstrate the potential of electrochemical sulfide abatement in sewers by demonstrating its working principle and the long term performance under realistic sewer conditions (see Appendix D for a detailed description of the experimental setup). The results showed that sulfide could be successfully removed to concentrations below 1 mg L^{-1} (i.e. target values), with average removal efficiencies for reactor A and B of $88 \pm 9\%$ and $76 \pm 30\%$, respectively (see Figure 4.4).

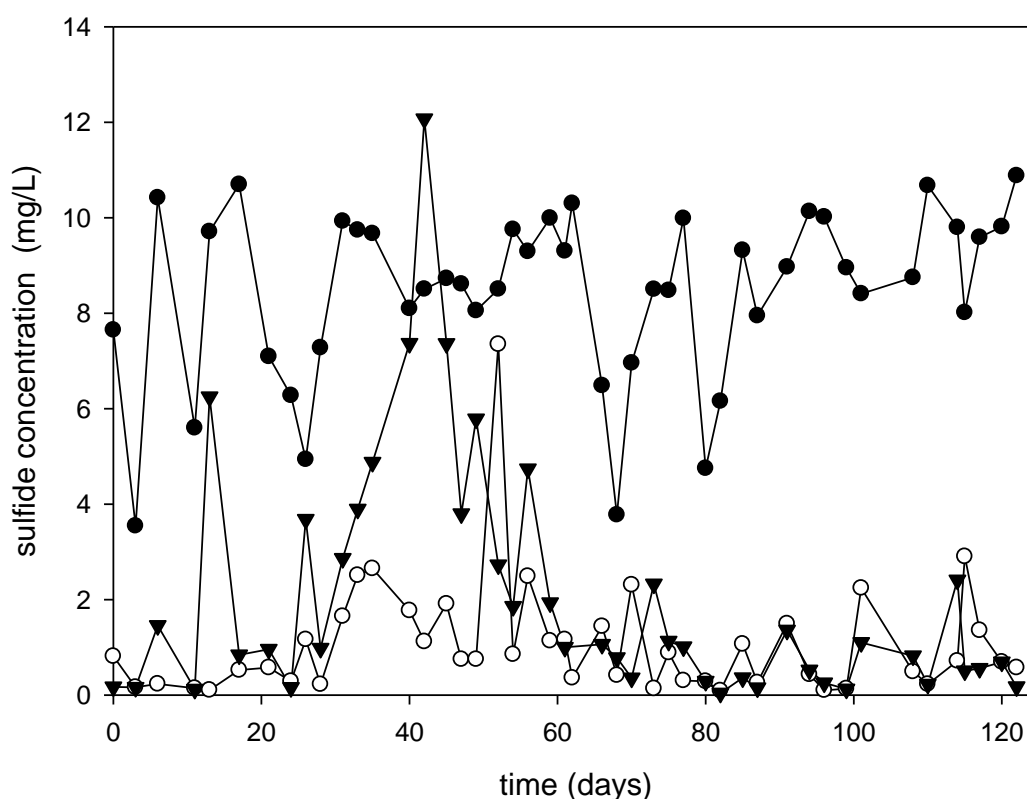


Figure 4.4. Sulfide-S influent (●) and effluents concentrations for reactor A (○) and reactor B (▼) over a period of 122 days.

A coulombic efficiency of $\sim 55\text{-}60\%$ for the generation of *dissolved* oxygen was obtained, compared to efficiencies often below 40% for conventional oxygen injection systems [32]. It appeared that the coulombic efficiency was not significantly affected by the current density applied, but mainly determined by the mixing intensity. This suggests that the generation of dissolved oxygen was limited by its diffusion into the liquid and not by the kinetics of oxygen formation at the electrode surface.

Over the course of the experiments the anode potentials were stable, while on the other hand, the cathode potentials significantly fluctuated over time. This was caused by fouling of the membrane as previously discussed in section 4.3. Periodic cleaning (i.e. ~once per week) of the cathode compartment with 0.05 M HCl acid solution was successful to remove the scaling from the electrode and membrane surface. In addition to this, the cathode potentials also returned to their original values at time there was a blockage in the anode feed line. As result of a blockage, there was no feed to the anode chamber, while protons were generated continuously thus generating an acid solution in-situ. Consequently, mainly protons were transported through the membrane to the cathode lowering the pH in the membrane slowly removing the scaling.

In a second stage, the feasibility of polarity switching every 2 days to overcome scaling issues was investigated. Figure 4.5 shows the profile of cathode potentials including ohmic losses (brown line) for reactor A (regular operation) and the cathode potentials with (orange line) and without ohmic losses (green line) for reactor B (polarity switching every 2 days) over a period of 34 days. Although a clear improvement of the cathode potential can be seen after every polarity switch, on average only a slightly improved (i.e. lower) cell voltage was observed with cathode potentials of -8.4 ± 1.4 and -7.3 ± 1.4 V for reactor A and B, respectively. Hence, in a practical situation a much more frequent switching of the polarity is required to minimize the energy requirements of the system.

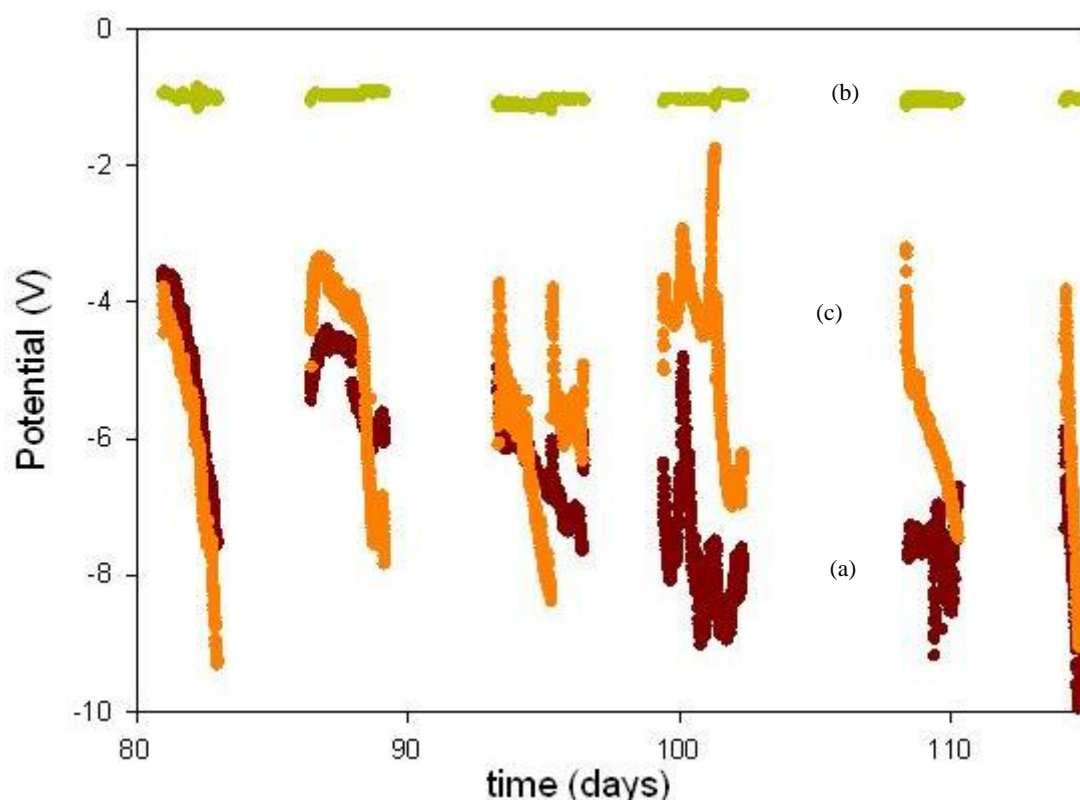


Figure 4.5. Cathode potentials including ohmic losses (brown (a)) of reactor A (regular operation) and the cathode (green (b)) and cathode potentials including ohmic losses (orange (c)) for reactor B (polarity switching) over a period of 34 days.

In addition to the efficiency of polarity switching, it is also important to realise that this can have a significant impact on the electrode life time. Also high pH values, which are especially observed when cathodic caustic generation becomes the desired abatement strategy, may reduce the electrode life time. The results showed that the electrode life time was significantly affected by the pH. The expected life time of the Pt/Ir electrode at pH 14 was approximately 6.0 ± 1.9 years, whereas at pH 12 the wear rate of the coating was very low (i.e. coating thickness is only slightly reduced) and thus higher electrode lifetimes can be expected (see Appendix D for a more detailed description of the methodology used to determine the expected electrode life time). In a practical situation, a divided reactor is used in which the electrodes are only exposed to a high pH in the cathode compartment, which is only 50% of the time. Thus, it is expected that this will increase the electrode life time even further. However, in a practical situation, also the presence of organics in sewage and mechanical wear (i.e. due to physical shear/friction of solids such as sand on the electrode surface) could have a negative impact on the electrode life time.

5. Conclusions and perspectives

5.1 Conclusions

The objective of this thesis was to develop a novel technology for sulfide abatement in sewer systems based on electrochemical oxidation/reduction. To investigate the feasibility of this new technology several laboratory scale experiments as well as field trials were performed. Different electrochemical approaches either based on (i) anodic processes (i.e. direct and indirect oxidation) or (ii) cathodic processes (i.e. hydrogen peroxide and caustic generation) were proposed and experimentally tested. Overall, the experimental results showed that caustic generation is the most cost-effective electrochemical approach. At the anode side, it was established that direct oxidation of sulfide was not feasible, and oxidation occurred mainly indirectly via electrogenerated oxygen (or other oxidants). Based on the current efficiency obtained and cell voltage applied, our cost calculation showed that the costs for sulfide abatement can be reduced from AUS \$2.5-9.4 kg S⁻¹ for conventional sulfide abatement strategies to AUS \$0.83-1.17 kg S⁻¹ for electrochemical sulfide abatement (see section 5.2.2). An additional advantage of in-situ generated caustic from sewage is that frequent transport, handling and storage of concentrated caustic, all constituting serious occupational health and safety hazards, are avoided. The more specific findings obtained during the different experimental studies are listed below:

a) Anodic sulfide oxidation

- (i) The experimental results showed that direct sulfide oxidation to elemental sulfur at the electrode surface is not feasible. The maximum obtainable limiting current density (mA cm⁻²) is linearly related to the sulfide concentration. Considering a target sulfide concentration of 1 mg L⁻¹, a too large electrode surface area would be required, which is practically not feasible.
- (ii) The main anodic reaction mechanism was sulfide oxidation by means of in-situ generated oxygen, and was independent of the electrode materials (i.e. Ta/Ir, Ru/Ir, Pt/Ir, PbO₂ and SnO₂ coated titanium) used. The latter was caused by the relatively low chloride and oxidisable pollutant concentration (i.e. organics and sulfide) present in sewage. The final products of oxidation were a mixture of sulfur species (i.e. sulfur, thiosulfate and sulfate).

- (iii) The presence of elevated chloride concentrations did not enhance the sulfide removal rate, whereas similar electron distributions among the different electron sinks were observed. There were no measurable amounts of chlorine present, but at this stage it cannot be excluded that significant amounts of chlorine were formed and instantly reacted with the sulfide or organics present in the sewage.
- (iv) The coulombic efficiency for *dissolved* oxygen generation using a Ta/Ir electrode was around 55-60%, and not affected by the current density applied. This is significantly higher than conventional oxygen injection systems with efficiencies normally below 40%.
- (v) The field trials showed that sulfide can be removed under real sewer conditions by anodic sulfide oxidation under the target value of 1 mg L^{-1} , with an average removal efficiency of $88 \pm 9\%$ over a period of 122 days. The cell potentials increased over time which was most likely caused by an increase in membrane resistance due to fouling of the membrane surface by precipitation of calcium and magnesium salts. Switching the polarity every 2 days was not sufficient to overcome these scaling issues.

b) Cathodic processes

- (i) A long term stable cathode process for the generation of hydrogen peroxide could not be achieved, which was most likely caused by blockage of the GDE by NaOOH or $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$. As sewage not only contains sodium, but also other cations such as calcium and magnesium, severe problems with scaling of the GDE can be expected.
- (ii) Caustic can be produced from sewage using Pt/Ir coated titanium electrodes at a current density of 10 mA cm^{-2} , with a coulombic efficiency of $53 \pm 8\%$ at an average cell voltage of $5.2 \pm 0.7 \text{ Volt}$. The decrease in coulombic efficiency was caused by cross-over of protons as well as back diffusion of hydroxyl ions, both processes being of similar importance.
- (iii) The use of spacers to increase the distance between anode and membrane surface, and thereby locally improving mixing conditions did not result in an increase in caustic recovery. However, it did results result in an increase in required cell voltage due to an increase in ohmic resistance of the system.
- (iv) Over time, the cell voltage increased due to an increase in resistance of the system caused by membrane fouling due to precipitation of calcium and magnesium salts.

Switching the polarity every four hours was successful to overcome these fouling issues, with cell voltages returning to their original values.

c) Electrode life time

- (i) Accelerated life time experiments showed that a life time of 6.0 ± 1.9 at pH 14 to ~39 years at pH 12 can be expected. This is based on continuous operation with polarity switching every 8 hours. The impact of organics and mechanical wear, which could also influence the electrode lifetime, was not taken into account. The life time of the electrodes if operated without polarity switching is expected to be even longer.

5.2 Perspectives

The laboratory scale experiments performed in this thesis showed the feasibility of electrochemical sulfide abatement. To successfully implement this technology at full scale, several process and engineering considerations, which were not trivial in the laboratory scale reactors, have to be taken into account. Therefore, the most critical process and engineering considerations are described in this paragraph. In addition, this paragraph also describes a case study to highlight the economic potential of electrochemical caustic generation from sewage as a sulfide abatement strategy. Lastly, the recommendations for future research and opportunities for electrochemical sulfide abatement strategies are discussed.

5.2.1 Determination of the most critical process and engineering considerations

The installation of an electrochemical reactor in a sewer application is subject to a number of restrictions posed by the working environment and the electrochemical requirements themselves. A workshop was organized with industry partners from the SCORE project, who are design experts in the field, to discuss the most critical process and engineering considerations with respect to the design of the electrochemical system. As we showed that the generation of caustic soda is a more cost-effective method than anodic sulfide oxidation, the process and engineering considerations are based on the implementation of an electrochemical cell for the generation of caustic soda (see section 4.6). With caustic soda generation being the desired process, the required flow rate in the anode (sewage) is determined by the amount of required cation transport (i.e. sodium or potassium) to the cathode to generate a caustic soda solution, and not the amount of electrons required for sulfide oxidation. As a result, it is not necessary to treat the complete sewage flow, and

therefore a side stream configuration can be implemented (see Figure 5.1). A side stream configuration has several advantages such as:

- The wastewater flow in the sewer system is independent of the electrochemical system. Therefore, in case of a malfunctioning of the system, the collection and transport of sewage in the sewer system is not affected;
- Since the design is not restricted to the dimensions of the sewer pipe it allows for such a design that reactor components (e.g. membrane and electrodes) can be removed and changed easily;
- The electrochemical cell can be stopped easily for maintenance by closing the valve of the inlet pipe;
- The inlet structure can be designed as such that in case of a blockage, it will occur at the inlet structure avoiding damage to the electrochemical cell;
- A sufficient upflow velocity in the inlet pipe can be applied to avoid large particles to enter the electrochemical cell;
- The system is less exposed to diurnal variations in flow regime as only a part of daily flow is treated.

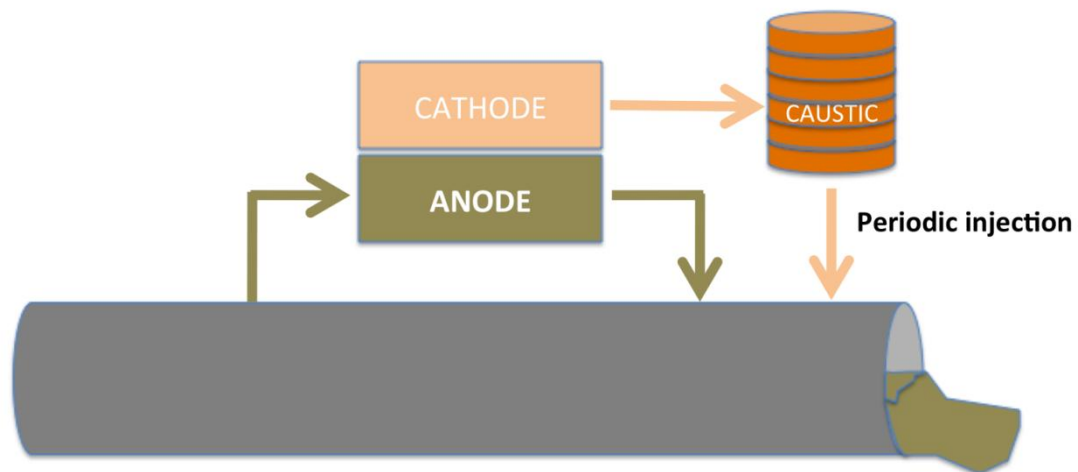


Figure 5.1. A simplified schematic overview of a side stream configuration for electrochemical caustic generation from sewage.

5.2.1.1 Engineering considerations

The design aims to avoid problems with (i) blockages, (ii) ragging, (iii) particle settling and accumulation, (iv) biomass accumulation on the electrode and membrane surface and (v) precipitation of inorganics. Blockage inside the electrochemical reactor should be avoided at all times to prevent damage to the reactor. Even if there is no damage, the electrochemical cell has to be opened, which will require human intervention and down-time of the system. To do so, the design must be such that large obstacles can freely flow through the electrochemical cell. Practical experience (personal communication Australian Water Boards) learns that blockage can be avoided if the dimensions are at least 50 mm. A blockage of the inlet structure, on the other hand, can easily be removed by switching the direction of the flow. Thus, the system should be designed such that in the rare occasion of a blockage (e.g. very large obstacle) it will affect the inlet structure and not the electrochemical cell itself. To further minimize the chance of a blockage, grinder/macerator pumps can be used. In this way, all larger parts will be grounded into smaller parts and hence clogging is significantly reduced, and most likely avoided at all times. A disadvantage of a grinder pump is a (slight) increase in energy requirements.

Ragging, by for example hair and tissues, will occur at every sharp or uneven point and therefore all components of the system must be curved and not have any bars, protrusions, sharp and uneven parts so hair and rags can rap around. Prevention of particle settling and accumulation can be avoided by applying a sufficient upflow velocity. In general, in rising mains an upflow velocity of at least 0.8 m s^{-1} is applied, which is sufficient to avoid any particle and biomass settling. Biomass accumulation on the electrodes will not happen, as the anode environment is not suitable for bacterial growth (strong oxidizing potential). Biomass accumulation on the membrane is avoided as the biomass is frequently exposed to elevated pH values due to frequent polarity reversal or to low pH low values when acid is produced in-situ.

The use of valves should be minimized, and if used, automated diaphragm valves should be used (personal communication Australian Water Boards). The frequency of switching the flow by the use of valves should be as low as possible to ensure stable operations. Valves are needed to (i) switch the direction of the flow of the inlet and outlet point of the rising main (in case of a blockage), (ii) harvest the caustic soda from the cathode compartment and (iii) switch the flow in the electrochemical cell in case polarity switching is used. It also is possible to only switch the direction of the current without changing the actual flow for a

short period by filling the cathode compartment with clean water (i.e. no buffer capacity). In this way, protons are produced in a small volume (i.e. pumps are not in operation in the cathode) and thus the pH decreases rapidly. This small stream can be discarded (or collected in a small buffer vessel) afterwards and the cathode can be filled with a clean stream again. The advantage of such a configuration is that a very small cathode compartment can be used (i.e. 1cm width) as it is never in contact with the sewage and no additional valves are needed for polarity switching, making it a very simple and compact construction. In figure 5.2AB schematic overviews of both configurations are presented.

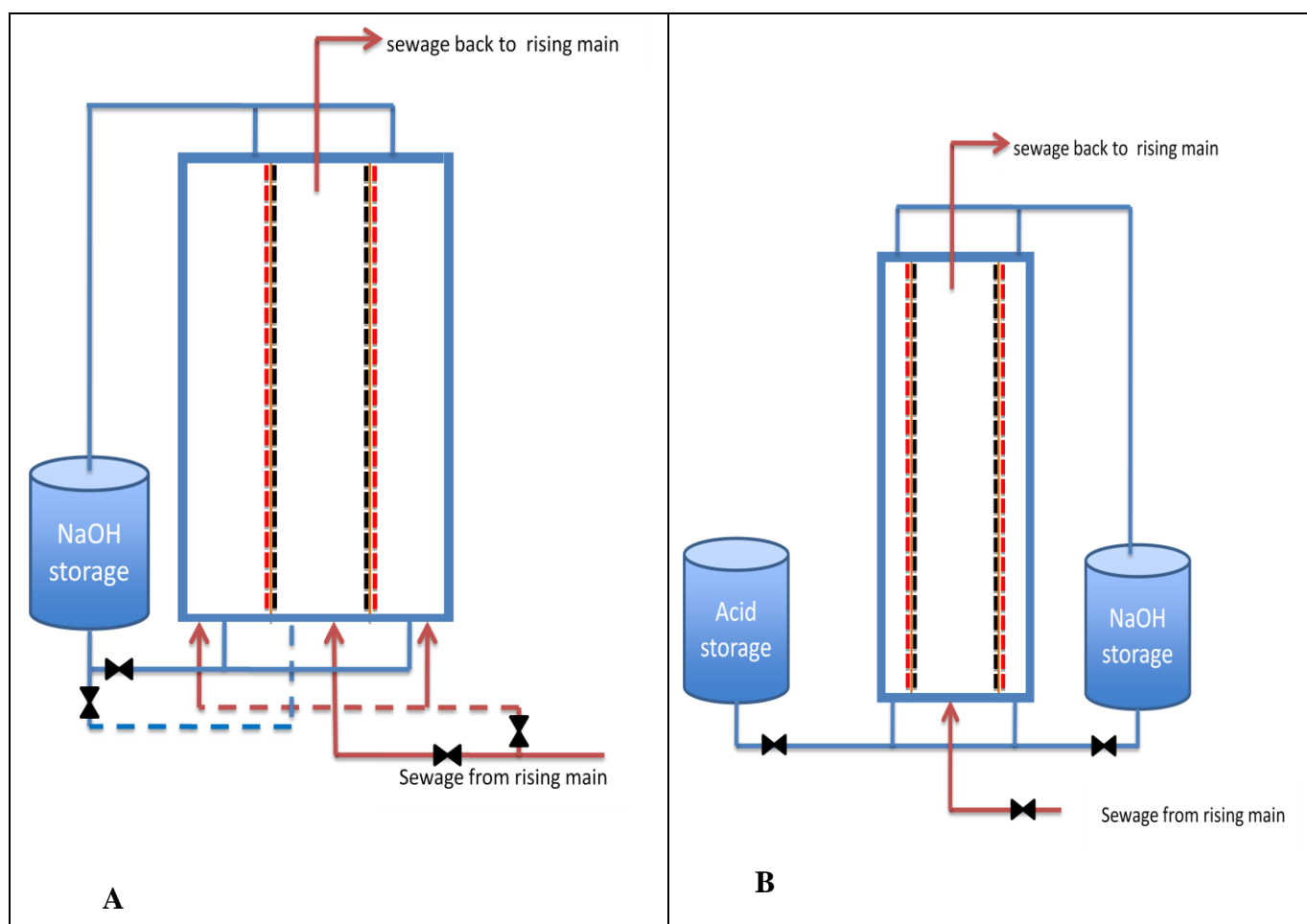


Figure 5.2. Simplified schematic overview of full scale configuration for electrochemical caustic generation from sewage. Red dotted line: cathode; black dotted line: anode; orange full line: membrane. Wastewater flows in from brown circuit, bottom to top. Produced NaOH is circulated over the cathode. Configuration (A): Polarity switching with changing the flow and configuration (B): polarity switching without changing the flow.

Alternatively, acid can be generated in-situ in the anode by operating the cell without any flow. This acid can then subsequently be fed to the cathode chamber to dissolve the scaling. This would allow for a system in which cheap cathode materials such as stainless steel or nickel can be used due to the absence of polarity switching, further reducing the costs of this new technology.

5.2.1.2 Process considerations

Sewer networks are often complex systems incorporating both rising mains and gravity sewers of different dimensions, lengths and daily flow. Wastewater flows through sewer networks vary significantly over time (day-night pattern), resulting in large fluctuations in HRT. In rising mains, the pumps are often turned on and off causing intermittent flow, with often long periods without any pumping events during night time. Considering the highest flow and thus minimal intermittent flow during day time, and the lowest flow and thus longest HRT during night time, the electrochemical cell only operates during day time. Once sufficient caustic has been produced over time (days), it can be dosed to the sewer during night time. In this way, long contact times of the caustic with the biofilm of the sewer pipes are achieved, thereby increasing its biocidal effectiveness. The required caustic dosage (and thus the reactor size and energy requirements) strongly depends on the diameter of the sewer pipe. Therefore, it becomes less attractive in rising mains with large diameter sizes. However, a very recent Australian industry survey reported that the diameter of the sewer pipe is <0.50 meter at ~94% of the sites currently dosing chemicals [163]. The length of the rising main also plays a role but is less important as the caustic dosage follows a plug-flow behaviour. As long as the pH drop due to CO₂ or other buffering along the pipe is not too significant, long pipes can be treated with one plug of caustic.

When only operated during day time, a solar panel can be used to drive the electrochemical cell. In this way, the system can be completely independent from the existing electrical grid. This can be an additional advantage, as the existing electrical grid, especially for pumping stations in remote areas, does not always provide sufficient power sources to enable operation of the electrochemical cell. Furthermore, in Australia, every Water Board (and industry) has to report on the greenhouse gas emissions from their water infrastructure. Hence, the use of a solar panel could significantly reduce the emission of greenhouse gases, making it a very sustainable solution. A life cycle assessment would provide more insight into the sustainability of this method compared to the existing abatement strategies. It

needs to be noted that using a solar panel will entail a higher operational cost due to the higher electricity costs.

In a full scale application, significant amounts of hydrogen gas can be generated in the cathode compartment. Therefore, dilution with air might be required to maintain hydrogen levels below its lower explosion limit (LEL). For this, air can be sparged into the cathode compartment. If sufficient air is provided, the reduction of oxygen to hydroxide can become an important reaction. In this way, hydrogen formation will be reduced and might even be avoided, depending on the amount of oxygen supplied and the current density applied. If more air is sparged into the cathode compartment, the energy requirements of the system will increase. However, the required cell voltage will decrease (i.e. the reduction of water under ambient pressures occurs at -0.42 Volt ($E^{0'}$) versus 0.815 Volt ($E^{0'}$) for the reduction of oxygen). This will at least partly compensate for the higher energy requirements caused by the increase in air supplied to the cathode.

5.2.2 Operating and capital costs

A cost calculation was performed to investigate the economic potential of electrochemical caustic generation from sewage as a means to prevent sewer corrosion. The cost calculation was based on a case study of the Elanora sewer network (Gold Coast, Australia) and the experimental results obtained in the laboratory scale experiments (see Appendix C). In Table 5.1 an overview of the characteristics of the Elanora sewer network is presented.

Table 5.1: Characteristics of the Elanora rising main case study (Gold coast, Australia).

parameter	unit	value
total lengths sewer pipe	m	± 20000
length to be filled	m	5000
diameter	m	0.53
volume sewer pipe	m^3	4330
flowrate sewer	$m^3 \text{ day}^{-1}$	14000

Recently, a field study showed that when caustic is dosed to the sewer network it follows a plug flow behaviour [63]. Hence, it is not necessary to completely fill the desired section of the sewer over the whole length to maintain elevated pH levels in all the sections of the pipe. It is assumed that filling 25% of the total volume of the sewer section is sufficient to maintain high pH levels throughout the whole sewer pipe. Laboratory scale experiments showed that a

pH of 10.5 for 2 hours is sufficient to deactivate the SRB present in the biofilm [65]. In the calculations a pH of 11.0 was used, as a small decrease in pH along the sewer pipe after the dosing point can be expected. In a practical situation, the caustic is dosed during night time to create sufficient HRT of the caustic in the sewer pipes. Normally, caustic is dosed every few days up to once per several weeks, depending on the local conditions and season (personal communication Australian Water Boards). It was assumed that a pH shock loading with a frequency of once a week is sufficient to prevent hydrogen sulfide generation. In Table 5.2 an overview of all the assumptions used in the calculation of the investment and operational costs are presented.

Table 5.2. Assumptions used for the calculation of the investment and operational cost for electrochemical caustic generation from sewage.

parameter	unit	value
lifetime electrodes	years	5-10
lifetime electrical and mechanical parts	years	10
% of total cost is electrode material ^{a)}	%	60%
cost anode material ^{a)}	dollar m ⁻²	1250
current density	mA cm ⁻²	10
coulombic efficiency for caustic generation	%	50
cost kWh	dollar kWh ⁻¹	0.10
required OH to reach pH of 11.0 ^{b)}	kg m ⁻³	0.4 ^{b)}
time of operation for caustic generation	hours per day	12
required frequency of dosing	per week	1
cell potential	Volt	6
sulfide concentration	mg L ⁻¹	10

a) Personal communication with supplier of electrochemical systems.

b) Dosage is based on titration curves during laboratory and field trials.

Table 5.3. The investments, operational and total costs for electrochemical caustic generation from sewage for sulfide abatement in sewer systems for the Elanora rising main system.

investment costs	unit	value
required anode surface area	m ²	69
total costs electrode (Anode + Cathode)	dollar	172,761
other costs ^{a)}	dollar	69,104
total costs electrochemical cell	dollar	241,865
operational costs (electricity)	unit	value
power input	W	41463
energy input	kWh day ⁻¹	498
energy costs	dollar year ⁻¹	18161
total cost (annual basis)	unit	value
total costs (electrode life time:10 years)	\$/m ³	0.008
	\$/kg S	0.83
total costs (electrode life time: 5 years)	\$/m ³	0.012
	\$/kg S	1.17

^{a)} Based on the assumption that the costs for the electrodes are 60% of the total cost of the electrochemical system (personal communication supplier electrochemical systems). This includes electrical parts, pumps and valves.

Recently, in a review paper of Zhang et al. (2008), it was reported that the cost for sulfide removal by chemical addition was €1.9-7.2 kg S⁻¹ [2], which is equal to AUS \$2.5-9.4 kg S⁻¹. These costs did not include the investment cost for the dosing equipment and storage of the chemicals. In a very recent Australian industry survey, it was shown that for chemicals most commonly used, the costs were AUS \$0.011 to \$0.17 per m³ sewage [64]. Considering an average sulfide concentration in sewage of 10 mg L⁻¹, this is equal to AUS \$1.1-17 kg S⁻¹ removed. Hence, our case study clearly shows the economic potential of electrochemical caustic generation from sewage as a means for sulfide control in sewers.

The accelerated life time experiments indicated that an electrode life time of at least 6.0±1.9 years (at pH=14) can be expected and significantly longer at lower pH values. Therefore, the cost calculation performed here is based on a rather conservative electrode and membrane service life of at least 5 years, a frequency of caustic dosage of once a week to fill 25% of the sewer pipe to pH 11 and the results obtained during laboratory scale experiments (i.e. cell voltage and coulombic efficiency). Long-term experiments (at least 12 months) at larger scale are needed to validate these process parameters and accurately assess the costs of this promising technique.

5.2.3 Recommendations for future research and opportunities

- (i) Our cost calculation showed that the costs for sulfide abatement can be reduced from AUS \$2.5-9.4 kg S⁻¹ [2] to AUS \$0.83-1.17 kg S⁻¹. Thus, we clearly showed the economic potential of electrochemical caustic generation from sewage as a solution to sewer corrosion (and odour problems). The cost calculation is based on the results obtained during laboratory scale experiments. Hence, the next step is to test this concept on a larger scale over a longer period (i.e. at least 1 year). Preferably, the experiments should be performed at such a scale that a complete rising main section can be treated. For example, a reactor with an anode surface of 3 m² would be enough to completely treat the UC09 rising main section of the Elanora sewer network (Gold coast, Australia), which has a length of 1 km and a diameter of 0.15 meter. UC09 has been used in the past during several field trials using different sulfide abatement strategies. Hence, this would allow us to compare the performance of electrochemical caustic generation to other sulfide abatement strategies under similar field conditions. The cell design and the long term performance in terms of coulombic efficiency for caustic generation, required energy input (i.e. cell voltage) and attainable caustic concentration will be critical parameters. The field trials should also give a good indication of the expected electrode and membrane life time under real sewer conditions.
- (ii) Switching the polarity of the electrodes every 4 hours was effective to overcome membrane fouling caused by precipitation of calcium and magnesium. Alternatively, an acid solution can be generated in the anode compartment by operating the cell without any flow for a short period of time. The produced acid solution can subsequently be pumped into the cathode chamber to dissolve the scaling. This would further reduce the costs of this technique as it would allow for a system in which cheap cathode materials such as nickel, titanium or stainless steel can be used. Furthermore, due to the absence of polarity switching the expected electrode life time will also be higher. Therefore, further research should focus on the feasibility of this method to overcome problems with membrane fouling.
- (iii) The experimental results showed that membrane fouling is a critical process parameter. Membrane fouling can never be completely avoided as calcium and magnesium are always present in sewage. However, it might be possible to reduce the rate at which membrane fouling takes place as it depends on several factors. For example, it has been

shown that the hydrodynamic conditions have an impact on membrane fouling in electro dialysis [164]. The use of monovalent cation exchange membranes, which theoretically should reject much of the bivalent cations, should prevent fouling. In practice, these membranes are however not monovalent, but they do possess a higher selectivity towards monovalent ions [165, 166]. In this way, the migrational transport of calcium and magnesium might be reduced, resulting in a decrease in the rate at which membrane fouling takes place. In addition, the applied flow rate and current density correspond to a certain anode-to-cathode-flux of cations through the membrane in order to maintain electroneutrality of the solution. By increasing the flow rate, and thus increasing the amount of sodium, the transport of calcium and magnesium might be reduced. Furthermore, scaling at the cathode might be reduced through the addition of anti-scaling agents in the cathode chamber. Hence, further research should aim to investigate the impact of (i) membrane choice, (ii) hydrodynamic conditions, (iii) the anode flow rate and (iv) the use of anti-scalant on membrane fouling rate.

- (iv) The above mentioned approaches are useful to reduce/minimize membrane fouling for practical applications on the short term. In addition to these engineering approaches, fundamental research should focus on the development of new membrane materials to completely solve the scaling issues on the long term. These fundamental studies should aim to improve the quality of the membranes in terms of (i) their selectivity towards monovalent ions and (ii) electrical resistance in low conductivity solutions (i.e. reduce the energy requirements of the system). Furthermore, microscopic studies should be performed to investigate the integrity of the membranes over time in detail. These studies should also aim to reveal the possible degeneration mechanisms responsible for aging of the membranes. In addition, voltammetry studies can be used to determine the electrical resistance of cation exchange membranes over time (e.g. new membrane and after being used for several weeks/months in the pilot studies).
- (v) Preferably, a highly concentrated caustic solution is produced as this would allow us to collect the produced caustic in a buffer tank with a small volume. However, the accelerated electrode life time experiments showed a significant impact of the pH on the electrode lifetime of Pt/Ir coated titanium electrodes with a decrease in electrode lifetime of a factor ~6 when increasing the pH from 12 to 14. Hence, there is clear relation between the electrode lifetime and the pH (i.e. obtained caustic soda concentration). Therefore, additional experiments should be conducted at different pH

values (e.g. 12.5, 13 and 13.5) to further elucidate the impact of the pH on the electrode life time.

- (vi) It is generally accepted that under polarity switching the electrode life time is reduced (e.g. the formation of titanium hydride layers) (personal communication with supplier of electrode materials). However, the specific mechanisms and conditions accelerating this phenomenon have not been studied in detail yet, and to the author's best knowledge are yet to be revealed. Therefore, it is of importance to fundamentally understand the specific mechanisms responsible and factors affecting the reduction in electrode lifetime. By varying the composition of the catalytic layer or the fabrication process, the resistance to polarity switching might be improved. This would allow for (i) better process control strategies to extend the electrode service life of existing catalytic coatings and (ii) the development of new catalytic coatings with a higher stability under polarity switching and high pH values.
- (vii) Electrochemical techniques for sulfide abatement are not restricted to sewer applications only. There is a variety of wastewater streams originating from industrial activities containing sulfide that are of interest. These include wastewater from tanneries and paper mills, spent caustics and geothermal brines. Sulfide present in geothermal brines that accompany oil and gas extraction is problematic as it causes corrosion of the metal pipes, as well as the release of obnoxious odours and its toxicity for workers [144]. In the petrochemical industry, spent caustics are formed during the removal of acidic compounds from gaseous streams and LPG. The transport and handling costs of spent caustics are currently very high and therefore treatment of these streams is economically attractive [164]. Sulfide present in wastewater from tanneries or the paper mill industry needs to be removed to allow discharge into waterways or sewer systems [10]. In general, sulfide is removed from the above mentioned waste streams by either (i) wet air oxidation at high temperatures and pressure or by (ii) chemical treatment by the addition of chemicals. Disadvantages of these methods are (i) high energy requirements (i.e. wet air oxidation), (ii) the formation of toxic sludge and (iii) the transport, storage and handling of chemicals. These disadvantages can be avoided if electrochemical techniques are used.

Contrarily to sewer systems, these industrial waste streams often have a high conductivity and moderate to high sulfide concentrations. For example, spent caustics often have a conductivity of $\sim 93 \text{ mS cm}^{-1}$ and sulfide concentrations of 240 mM (i.e.

$\sim 7.7 \text{ g L}^{-1}$) [164], whereas the sulfide concentration in geothermal brines often reach 60 mM [146]. In addition, these streams are often low in suspended solids allowing the use of cheap carbon based materials with a high surface area (e.g. graphite granules). Hence, for these waste streams, selective oxidation of sulfide to elemental sulfur at the electrode surface seems an attractive option. Until now, the potential application of electrochemical techniques to treat the above mentioned waste streams have been poorly studied. Recently, the working principle and economic potential of sulfide oxidation and recovery from paper mill anaerobic treatment effluent during laboratory scale experiments was shown by our laboratory [10]. Hence, this shows the potential of electrochemical techniques for the abatement of problematic wastewaters containing sulfide.

- (viii) In case selective sulfide oxidation to elemental sulfur at the electrode surface is the preferred option, cheap carbon based materials (e.g. graphite granules) can be used. So far, in the few studies that have been performed, mainly graphite granules or carbon brushes were used. Therefore, research should focus on the feasibility of different carbon materials to determine the most suitability anode materials for selective sulfide oxidation. For example, electrospun fiber mats with a very high specific surface area were recently proposed as anode material in MFCs [167] and seem promising for sulfide oxidation due to their high specific surface area. Furthermore, research is needed that seeks to modify the surface of these materials by different surface pre-treatment in order to improve the electrode kinetics (i.e. increase in catalytic activity towards sulfide oxidation) or conductivity of the materials.
- (ix) Wastewaters rich in organics are normally anaerobically treated in which biogas is produced. During anaerobic treatment, hydrogen sulfide is often formed and accumulates in the produced biogas. Hydrogen sulfide needs to be removed from biogas prior to its use, due to its corrosive nature [168]. In addition, removal of hydrogen sulfide is also often needed from landfill gas [169]. Here, the implementation of a BES system can be a very interesting option as organics can be removed in the anode, while generation a caustic solution in the cathode. The produced caustic can be used to absorb the sulfide from the biogas. If an anion exchange membrane is used, the absorbed sulfide is transported from the cathode to the anode compartment where it is oxidized. In absence of organics, also a direct electrochemical process can be used.

- (x) Another possible application is an electrochemical system in which a sludge liquor solution (i.e. excess sludge from an activated sludge system) is constantly recirculated over the anode compartment while feeding the cathode with biogas. This creates a low pH in the anode due to the proton generation during the oxidation of water, while generating a caustic solution at the cathode adsorbing the sulfide from the biogas. Hence, the sludge will undergo lyses due to the low pH in the anode, lowering the excess sludge production of a conventional activated sludge system. This might be an interesting option for countries in which sludge has to be incinerated (e.g. Netherlands).

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APPENDIX A

Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities

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Abstract

Hydrogen sulfide generation is the key cause of sewer pipe corrosion, one of the major issues in water infrastructure. Current abatement strategies typically involve addition of various types of chemicals to the wastewater, which incurs large operational costs. The transport, storage and application of these chemicals also constitute occupational and safety hazards. In this study, we investigated high rate electrochemical oxidation of sulfide at Ta/Ir mixed metal oxide (MMO) coated titanium electrodes as a means to remove sulfide from wastewater. Both synthetic and real wastewaters were used in the experiments. Electrochemical sulfide oxidation by means of indirect oxidation with in-situ produced oxygen appeared to be the main reaction mechanism at Ta/Ir MMO coated titanium electrodes. The maximum obtained sulfide removal rate was $11.8 \pm 1.7 \text{ g S m}^{-2} \text{ projected anode surface h}^{-1}$ using domestic wastewater at sulfide concentrations of $\geq 30 \text{ mg L}^{-1}$ or higher. The final products of the oxidation were sulfate, thiosulfate and elemental sulfur. Chloride and acetate concentrations did not entail differences in sulfide removal, nor were the latter two components affected by the electrochemical oxidation. Hence, the use of electrodes to generate oxygen in sewer systems may constitute a promising method for reagent-free removal of sulfide from wastewater.

keywords: sewer corrosion, electrochemical systems, sulfide oxidation, in-situ oxygen generation

1. Introduction

Hydrogen sulfide is ubiquitously found in domestic and industrial wastewaters [1]. It is a toxic, corrosive and odorous compound, often requiring removal from the aqueous or gaseous phase before discharge into the environment. Hydrogen sulfide is of particular concern in sewer systems since it causes corrosion of sewer pipes. Current technologies for sulfide abatement in sewer systems involve adding chemicals to wastewater to prevent sulfide formation, or its transformation from liquid to gas phase [2]. The commonly used chemicals include oxidants such as oxygen [3, 4] and nitrate [5, 6] for sulfide oxidation, iron salts for sulfide precipitation [7-9] and magnesium hydroxide to elevate pH [4, 10]. Other chemicals used include chlorine, hydrogen peroxide, caustic and nitrite, which are toxic to sewer biofilms [4, 11]. These strategies are considered expensive ($\$1.7\text{-}7.2 \text{ kg S removed}^{-1}$) [4] and often come with a number of limitations such as sludge generation or loss of organics, the latter are needed for nutrient removal in downstream WWTPs.

Recent advances in electrode development and operation have increased the interest in electrochemical abatement strategies. Electrochemical techniques offer several advantages including no requirement for dosing, transport and storage of hazardous chemicals, robustness, versatility, controllability and the amenability to automation [12]. A typical electrochemical reactor consists of an anode, a cathode and a membrane separating both. At the anode, electrochemical oxidation of a pollutant (here sulfide) can be achieved. Electrochemical oxidation can either be achieved by direct oxidation at the electrode surface or by indirect oxidation. During indirect electrochemical oxidation, oxidants including OH^\bullet , O_2 and Cl_2 , are generated at the anode surface; these subsequently oxidize the pollutant in the bulk solution. The reaction mechanism and selectivity of the oxidation process is mainly determined by the electrode material, the flow regime and the applied anode potential. Thus, depending on the conditions, sulfide can be oxidized at the anode or oxidized by in-situ generated oxidants. Sulfide can be oxidized to elemental sulfur, thiosulfate or sulfate. The oxidation of sulfide to sulfur is preferable since this requires the least amount of electrons and thus energy input [13].

A number of studies on aqueous electrochemical sulfide oxidation have been performed in the past [1, 13-18]. However, most of these studies reported on the direct oxidation of sulfide to elemental sulfur at carbon based anode materials using high strength/conductivity solutions such as alkaline media and brine solutions, at high sulfide concentrations and predominantly operated at low current densities [13-16]. However, for sewer systems, low current densities

using high surface area carbon based electrodes are not feasible due to the large reactor size that would be required. Domestic wastewater typically has a sulfide content of around $\sim 10 \text{ mg HS}^- \text{ L}^{-1}$, which is much lower than the concentrations tested in the aforementioned studies [19]. Furthermore, since the electrochemical cell has to treat raw unfiltered sewage, flat mesh shaped electrodes are needed to avoid blockage and ragging of the system. Taking into account the low sulfide concentration and the use of flat mesh shaped electrodes (low surface area) indirect electrochemical reactions are likely to play a dominant role due to the limited reactant availability at the electrode surface.

IrOx coated titanium electrodes are extensively used as oxygen evolution electrodes in electroflotation and electrocoagulation reactors [20]. Miller and Chen reported on the direct anodic sulfide oxidation using titanium based $\text{Ti/Ta}_2\text{O}_5\text{-IrO}_2$ electrodes from a caustic medium [21]. This implies that, depending on the operational conditions (e.g. anode potential, sulfide concentrations), simultaneous sulfide oxidation and in-situ oxygen generation should be achievable. This oxygen can be used as a downstream control measure by either inhibiting the activity of sulfate reducing bacteria (SRB) and/or the oxidation of the sulfide that has been produced [3]. The kinetics and stoichiometry of the oxidation of sulfide by oxygen is well described in literature [19, 22].

Therefore, the aim of this study was to examine the feasibility of simultaneous oxidation of aqueous sulfide to elemental sulfur and water to oxygen at high current densities, using defined synthetic feed and domestic wastewater and a Ta/Ir MMO coated titanium electrode as anode.

2. Materials and Methods

2.1 Electrochemical cell and operation

The two-chambered electrochemical cell consisted of two parallel Perspex frames (internal dimensions $14 \times 12 \times 2 \text{ cm}$) separated by a cation exchange membrane (Ultrex CM17000, Membranes International Inc., USA). In the anode chamber, a mesh shaped Ta/Ir MMO ($\text{TaO}_2 / \text{IrO}_2$: 0.35/0.65) coated titanium electrode with a projected surface area of 100 cm^2 was used (Magneto Anodes BV, The Netherlands). Stainless steel fine mesh (168 cm^2) with a stainless steel current collector (6 mm mesh size, 0.8 mm wire) was used as electrode material in the cathode chamber. The anode liquid medium was constantly recirculated over an external buffer vessel, allowing a total anode liquid volume of 5 L. We operated the

reactors in fed batch mode, as a once through system would have required cubic metre volumes of defined media/sewage per day to enable operation of the reactors at the desired current densities. The latter was not practical in the laboratory. The disadvantage of this recirculatory mode, however, is that the “influent” sulfide concentration into the reactor will slowly increase if 100% removal efficiency is not achieved. In the experiments, the sulfide concentrations increased to 30 to $\sim 90 \text{ mg L}^{-1}$, depending on the current applied and anode medium used, as the experiments progressed. An example of the typical sulfide concentration profile during the course of the experiments is shown in Figure 4.

The influent flow rate through the anode chamber was maintained at 15 L h^{-1} using a peristaltic pump (Watson Marlow, UK). The off gas coming from the external buffer vessel was sent through a water-lock containing a 0.2 M NaOH solution. The recirculation flow in the anode chamber was kept at 22 L h^{-1} using a peristaltic pump (Watson Marlow, UK) to obtain a higher mixing rate in the anode chamber. PVC tubing with an internal diameter of 4.5 mm was used for the feeding and recirculation lines.

In all experiments, an Ag/AgCl (RE-5B, Bio Analytical, USA) was used as the reference electrode. Its potential was estimated at $+197 \text{ mV}$ versus standard hydrogen electrode (SHE).

An external buffer flask of 2 L was used in the recirculation of the cathode chamber. A 0.1 M NaOH solution in the cathode chamber was used in all experiments to trap any possible crossover of hydrogen sulfide. The recirculation flow of the cathode solution was kept at 22 L h^{-1} using a peristaltic pump (Watson Marlow, UK). Experiments were initially performed using a defined synthetic feed (with composition to be described later) and subsequently domestic wastewater. Both for the synthetic and real domestic wastewater experiments, sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was supplied continuously to the incoming line of the anode chamber via a syringe pump (NE-1600, New Era Pump Systems, Inc., USA) at a dosing rate of $149 \pm 20 \text{ mg S h}^{-1}$, i.e. sufficient to give an anode influent concentration of $\sim 10 \text{ mg S L}^{-1}$. Before use, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ crystals were washed with milliQ ($18 \text{ M}\Omega$) water to remove oxidized sulfur species on the surface of the crystals [1]. Due to the production of protons at the anode, a decrease of the anode pH is expected over time. To compensate for this, NaHCO_3^- was added (5 g L^{-1}) in the experiments using synthetic feed to maintain pH values commonly found in sewer systems. As the buffer capacity of domestic wastewater was not sufficient the pH was maintained at 7.5 by a PLC controlled dosage of a 0.5 M NaOH solution. The latter is not required in a practical situation since there a once through system would be implemented. An overview of the experimental setup is presented in Figure 1.

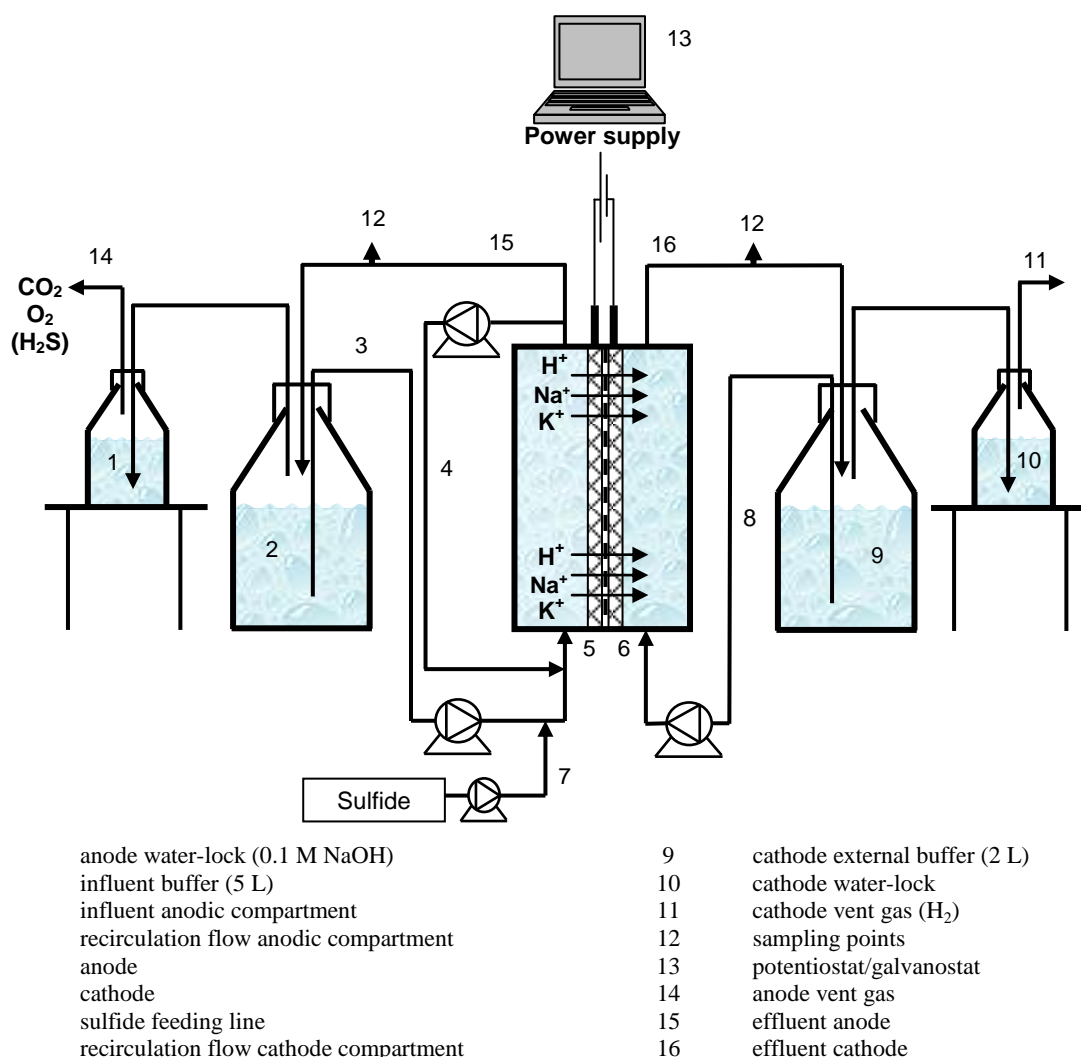


Fig. 1. Schematic overview experimental setup

2.2 Measurements and calculations

Galvanostatic measurements and controls were performed using a Wenking potentiostat/galvanostat (KP07, Bank Elektronik GmbH, Germany). The anode potentials and the current were recorded every 60 seconds using an Agilent 34970A data acquisition unit. All calculations were performed according to Logan et al and Rabaey et al [23, 24]. Coulombic efficiencies were determined on the basis of sulfide to elemental sulfur conversion.

2.3 Experimental procedures

Experiments, divided into 4 different sets, were conducted to verify the feasibility of electrochemical sulfide oxidation at high current density from synthetic and real domestic wastewater. Each time, the performance was assessed in 6 hour experimental runs using

galvanostatic control at different current densities. During the experiments with continuous sulfide dosing, sulfide was fed at a rate of $149 \pm 20 \text{ mg S h}^{-1}$ to the reactor during six hours. This is equivalent to a loading rate of $444 \pm 60 \text{ mg S L}^{-1}_{\text{anode volume}} \text{ h}^{-1}$, or a current (density) of $\sim 250 \text{ mA}$ (25 A m^{-2}) (i.e., based on a 2-electron oxidation of sulfide to elemental sulfur). Prior to every run, the Ta/Ir MMO coated titanium electrode was rinsed in an alkaline sodium sulfide solution to remove deposited elemental sulfur (i.e. formation of soluble polysulfides) and subsequently rinsed with miliQ ($18 \text{ M}\Omega$) water to remove any aqueous (poly)sulfides left in the electrochemical cell. Aqueous sulfur species (i.e. sulfide, sulfite, thiosulfate and sulfate), acetate and COD concentrations were measured in 1.5 hours intervals during the continuous experiments and every 1 hour during the batch experiments. IC analysis of the anode water-lock was performed at the end of every experiment to account for the amount of any H_2S stripped from the buffer vessel.

IC analysis of the cathode compartment was performed during initial experiments to determine possible transfer of H_2S gas from the anode to the cathode through the membrane. These results indicated negligible transfer of H_2S from anode to cathode, which is in agreement with [1] and with what would be expected from a cation exchange membrane (as sulfide is an anion). Therefore, in the experiments from thereon it was assumed that no transfer of H_2S through the membrane occurred.

2.3.1 Experiment 1

In the first set of experiments synthetic feed was used to determine the impact of current density on the kinetics on the sulfide oxidation process and the final products of sulfide oxidation. Experiments were performed in triplicate at fixed current densities of 25, 50 and 100 A m^{-2} , respectively.

2.3.2 Experiment 2

In the second set of experiments, synthetic feed was used to investigate the impact of the presence of alternative electron donors (i.e. acetate) and chloride. Furthermore, trace elements in concentrations normally found in domestic wastewater, were added to investigate their catalytic effect (i.e. catalysts for auto-oxidation of sulfide) on chemical sulfide oxidation with in-situ oxygen generation. Trace elements composition and concentrations normally found in domestic wastewater were used according to Rabaey *et al.* [25]. Two different experiments were performed: (a) sulfide oxidation in presence of trace elements and the

absence of both acetate and chloride (in triplicate), (b) sulfide oxidation in the presence of acetate ($424 \pm 8 \text{ mg L}^{-1}$), chloride ($170 \pm 5 \text{ mg L}^{-1}$) and trace elements (in quintuplicate). Experiment (a) was performed at a fixed current density of 50 A m^{-2} to investigate their catalytic effect on chemical sulfide oxidation with in-situ oxygen generation whereas experiment (b) was performed to investigate if organics (e.g. acetate) and/or chloride (i.e. in-situ production of chlorine) are electrochemically oxidized during sulfide oxidation.

2.3.3 Experiment 3

The third set of experiments was performed (in quintuplicate) at a fixed current density of 50 A m^{-2} to determine the kinetics, coulombic efficiency and reaction products of sulfide oxidation in domestic wastewater.

2.3.4 Experiment 4

The fourth set of experiments was performed to investigate the oxidation kinetics of sulfide at concentrations close to 1 mg L^{-1} (i.e. target concentration in sewer systems). Therefore, batch tests were performed (in triplicate) using domestic wastewater at a fixed current density of 50 A m^{-2} spiked with sulfide to obtain an initial concentration of ($8.3 \pm 0.75 \text{ mg L}^{-1}$).

2.4 Chemical analyses

Sulfide, sulfite, thiosulfate and sulfate concentrations were measured with Ion Chromatography (IC), using the Dionex 2010i system, according to Keller-Lehman *et al.* (2006) [26]. Samples collected from the reactors were immediately filtered by a $0.22 \text{ }\mu\text{m}$ syringe filter (Millipore, USA) and preserved in previously prepared Sulfide Antioxidant Buffer (SAOB) solution prior to ion chromatography analysis. SAOB solution was also used to dilute the samples when necessary. SAOB solution was prepared using nitrogen purged MilliQ ($18 \text{ M}\Omega$) water, 3.2 g L^{-1} NaOH and 2.8 g L^{-1} α -ascorbic acid. After preparation, the solution was kept refrigerated, shielded from light and not used beyond 24 hours.

Sulfide concentrations were also measured with a handheld ion selective electrode for sulfide measurements (Sentek, Sentek Type 3225, United Kingdom). Samples from the reactor were immediately filtered by a $0.22 \text{ }\mu\text{m}$ syringe filter (Millipore, USA) and preserved in previously prepared Sulfide Antioxidant Buffer (SAOB) to obtain a SAOB to sample ratio of 1:1. SAOB solution was prepared using nitrogen purged MilliQ ($18 \text{ M}\Omega$) water, 80 g L^{-1}

NaOH, 67 g L⁻¹ EDTA and 35 g L⁻¹ α-ascorbic acid (as recommended by supplier). Calibration curves were obtained by combining the sulfide concentrations from IC analysis with the observed redox potentials using the ion selective electrode. In this way, possible drift of the electrode is ruled out since the electrode is internally calibrated every time an analysis is performed.

COD concentrations were determined by means of COD cuvette tests (Merck, range 25-1500 mg L⁻¹). Volatile fatty acids (VFAs) concentration was determined by High Performance Liquid Chromatography (HPLC). The pH was either controlled online or measured using a hand-held meter (Cyberscan PC 300, Eutech Instruments).

Produced gas was collected in gas collection bags (SKC Tedlar 1 Liter Sample Bag). The collected gas was analysed for O₂ concentrations using a gas chromatograph (Shimadzu, molecular sieve, stainless steel, 6 ft × 1 × 8" OD).

3. Results

3.1 Sulfide oxidation from synthetic feed in the absence of trace elements, chloride and acetate

The results of the experiments from synthetic feed at current densities of 25, 50 and 100 A m⁻² are detailed in Table 1. The sulfide removal rates increased from 6.1±0.3 to 9.2±0.4 g S m⁻² anode surface h⁻¹ when the current density was increased from 25 to 100 A m⁻². Figure 2A shows the total amount of sulfide removed (mg S) at the applied current densities. Increasing the current density from 50 to 100 A m⁻² did not result in significantly higher sulfide removal rates. However, it did result in higher gas production, indicating more oxygen was produced in-situ.

The pH at the start of all experiments using synthetic wastewater was 8.3. As oxidation progressed, the pH decreased to ~7 due to the release of protons generated as the sulfide is removed from the solution. The observed in-situ gas production (i.e. oxygen) at current densities of 25, 50 and 100 A m⁻² were 319±1, 808±29 and 1843±64 mL, respectively, which is higher than the maximum attainable oxygen (i.e., 343.75, 687.5 and 1375 mL) if all electrons are used for oxygen generation. Analysis of the gas composition performed in the second set of experiments confirmed that the extra gas produced originated from stripping of CO₂. Over the course of the experiments the anode potentials remained fairly constant.

Table 1. Sulfide oxidation from synthetic feed at current densities of 25, 50 and 100 A m⁻² using a NaHCO₃⁻ buffer solution

parameter	unit	value		
current density	A m ⁻²	25	50	100
coulombic efficiency	%	44±3	30±5.5	14.3±0.8
removal rate	mg S h ⁻¹	63.5±5	80.7±11	98.9±10
	mg S m ⁻² anode surface h ⁻¹	6.06±0.25	8.13±1.26	9.16±0.37
SO ₃ -S produced	%	6.4±3.0%	3.5±1.6%	2.4±0.7%
S ₂ O ₃ -S produced	%	25.8±6.9%	21.3±3.6%	9.8±0.6%
SO ₄ -S produced	%	36.1±7.7%	36.1±3.5%	27.1±2.9%
S ⁰ produced ^{a)}	%	29.3±17.2%,	38.3±5.3%	53.6±1.3%
gas production	mL	319±1	808±29	1843±64

a) The difference in sulfide-S added and sulfide-S removed (i.e., oxidized to SO₃-S, S₂O₃-S and SO₄-S) was assumed to be elemental sulfur present in solid form or in soluble form as polysulfide.

3.2 Sulfide oxidation from synthetic feed in presence of (a) trace elements and (b) trace elements, acetate and chloride

The results of the experiments from synthetic feed at a current density of 50 A m⁻² in the presence of trace elements, chloride and acetate are detailed in Table 2. The average obtained sulfide removal rate was 10.9±0.6 in the presence of trace elements and 11.2±1.6 g S m⁻² anode surface h⁻¹ in the presence of trace elements, chloride and acetate, respectively. This was 34±13% and 37±18% higher than the removal rate obtained with synthetic feed without (a) trace elements and (b) acetate, chloride and trace elements. Figure 2B shows the total amount of sulfide removed (mg S) in the presence of (a) trace elements and (b) trace elements, acetate and chloride at a fixed current density of 50 A m⁻².

Acetate analysis confirmed that acetate was not significantly removed (i.e., 1.9±3.0%). The presence or absence of chloride did not result in either an increase or decrease in obtained sulfide removal rate. Analysis of the gas composition showed that 35.4±1.2 mg hr⁻¹ of excess oxygen was generated. In Table 3 a summary of the electron balance is presented.

Table 2. Sulfide oxidation from synthetic feed in (a) absence of trace elements, acetate and chloride, in presence of (b) trace elements and (c) trace elements, acetate, and chloride and (d) domestic waste water at a current density of 50 A m⁻²

parameter	unit	HCO ₃ ⁻ buffer solution	trace elements	trace elements, acetate and chloride	domestic waste water
coulombic efficiency	%	30±5.5	32%±1	33%±2	40%±2
removal rate	mg S h ⁻¹	80.7±11	123.5±0.6	129±12	136±18
	mg S m ⁻² anode surface h ⁻¹	8.13±1.26	10.86±0.6	11.38±1.15	11.76±1.68
SO ₃ -S produced	%	3.5±1.6%	4.1±1.1	2.8±1.3	2.1±0.9
S ₂ O ₃ -S produced	%	21.3±3.6%	32.4±0.6	34.4±4.9	62.4±11.1
SO ₄ -S produced	%	36.1±3.5%	26.1±1.2	28.8±5.2	13.9±4.6
S ⁰ produced ^{a)}	%	38.3±5.3%	37.0±1.7	44±22	21.6±14.4
acetate removal	%	n.d.	n.d.	1.9±3	9±4
gas production	mL	808±29	800±70	750±4	283±5
oxygen produced	mg	not measured	not measured	212±7 ^{b)}	76±6 ^{b)}

^{a)} The difference in sulfide-S added and sulfide-S removed (i.e., oxidized to SO₃-S, S₂O₃-S and SO₄-S) was assumed to be elemental sulfur present in solid form or in soluble form as polysulfide.

^{b)} Measured in duplicate.

3.3 Sulfide oxidation from domestic wastewater

The results of the experiments from domestic waste water at a current density of 50 A m^{-2} are detailed in Table 2. The average obtained sulfide removal rate was in the same order as the removal rates obtained from synthetic feed in the presence of trace elements (i.e. 11.8 ± 1.7 versus 10.9 ± 0.6 and $11.2 \pm 1.6 \text{ g S m}^{-2} \text{ anode surface h}^{-1}$). Analysis of the gas composition showed that $13 \pm 1 \text{ mg hr}^{-1}$ of oxygen was produced. COD analyses revealed that the average COD removal was $9 \pm 4\%$. During the experiments the anode potentials remained fairly constant at $3.4 \pm 0.4 \text{ Volt}$. In Table 3 a summary of the electron balance is presented.

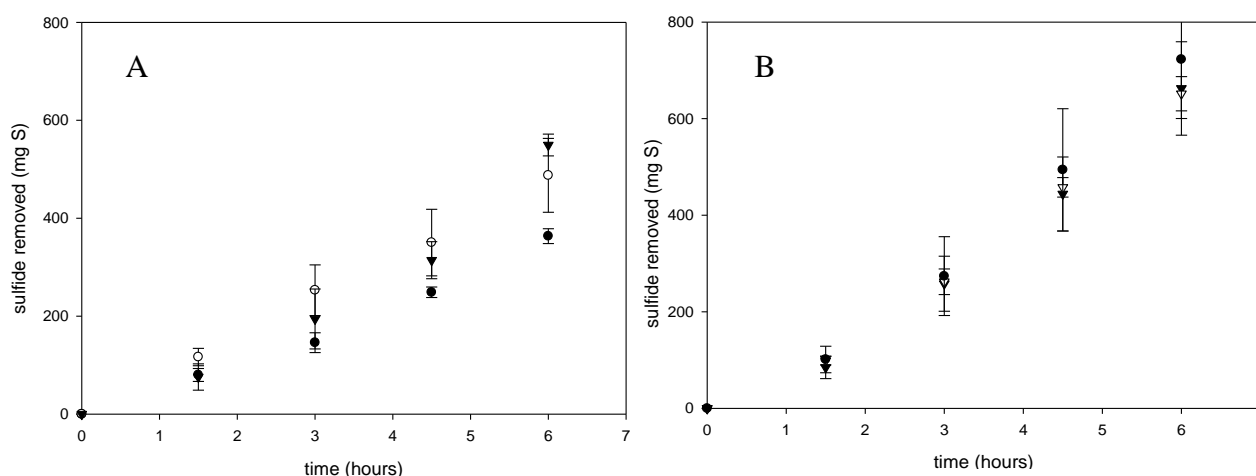


Fig. 2A. Comparisons of the amount of sulfide removed (mg S) in the absence of trace elements, acetate and chloride at fixed current densities of 25, 50, 100 A m^{-2} ($n=3$): (\bullet) 25 A m^{-2} , (\circ) 50 A m^{-2} and (\blacktriangledown) 100 A m^{-2} . **Fig. 2B.** Comparisons of the amount of sulfide removed (mg S) in the presence of (∇) trace elements ($n=3$), (\blacktriangledown) trace elements, acetate and chloride ($n=5$) and (\bullet) domestic wastewater ($n=5$) at a fixed current density of 50 A m^{-2} .

3.4 Batch test for sulfide oxidation at low concentrations

The results of the batch tests for sulfide oxidation at low concentrations at a fixed current density of 50 A m^{-2} are shown in Figure 3. The average sulfide removal rate was $16.8 \pm 5.0 \text{ mg S h}^{-1}$, which is equal to a removal rate of $1.7 \pm 0.5 \text{ g S m}^{-2} \text{ anode surface h}^{-1}$, approximately one eighth of the removal rates obtained during the continuous experiments.

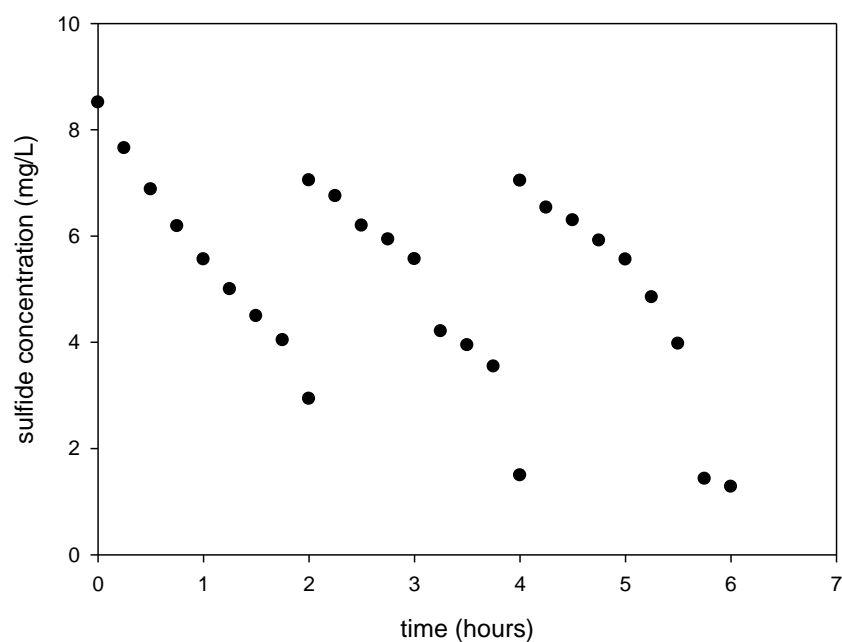


Figure 3. Sulfide concentration (mg L^{-1}) profile using at a current density of 50 A m^{-2} using domestic wastewater spiked with sulfide.

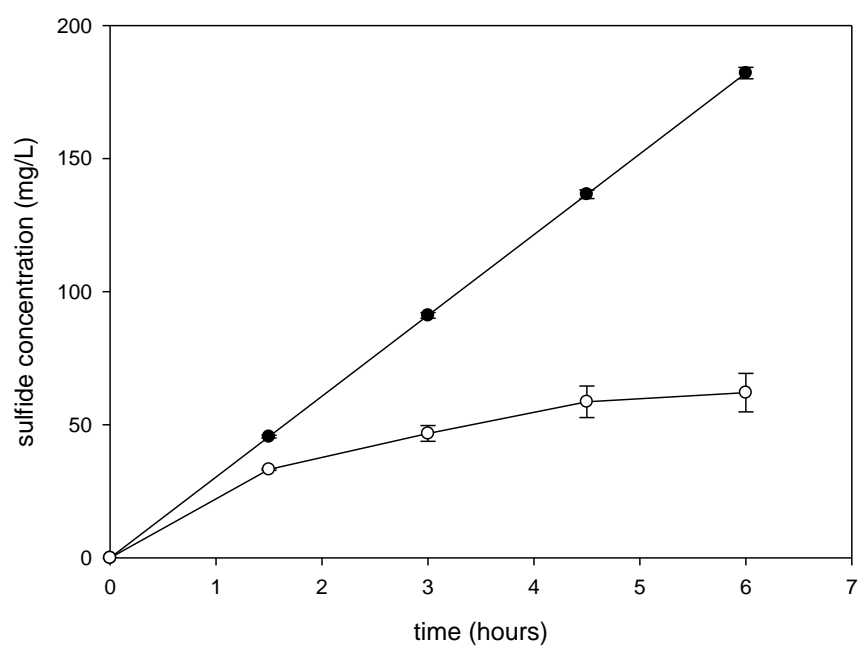


Figure 4. Typical sulfide generation profile during galvanostatic control at a current density of 50 A m^{-2} in the presence of acetate, chloride and trace elements ($n=3$): (●) sulfide dosed (mg L^{-1}) and ○ sulfide concentration.

4. Discussion

4.1 Sulfide oxidation and in-situ oxygen generation

In this work, we investigated the simultaneous aqueous sulfide oxidation and in-situ oxygen generation using Ta/Ir MMO coated titanium electrodes. The impact of organics (i.e. acetate), chloride and trace elements on the kinetics on sulfide oxidation and in-situ oxygen generation was successfully investigated.

To investigate the kinetics of sulfide oxidation at low concentrations, batch experiments with low sulfide concentrations were performed as well. Aqueous sulfide removal by electrochemical oxidation with concomitant in-situ oxygen generation was demonstrated using defined synthetic media as well as domestic wastewater.

Increasing the applied current from 50 to 100 A m⁻² did not proportionally enhance sulfide oxidation, hence the coulombic efficiency decreased. The higher current caused more diversion of the electrons towards gas production (oxygen), which in a practical situation can be used for downstream sulfide control (i.e., prevention of sulfate reduction) or aqueous phase based sulfide oxidation [3, 27]. The expected sulfide oxidation rate (mg S L⁻¹ h⁻¹) from domestic wastewater with pure oxygen at a sulfide concentration of 30 mg L⁻¹ and a dissolved oxygen concentration of 40 mg L⁻¹ would be 28.7 mg S L⁻¹ h⁻¹ [28]. The observed sulfide removal rate in the experiments using domestic wastewater was 23.5±3.0 mg S L⁻¹ h⁻¹, indicating indirect oxidation of sulfide with in-situ generated oxygen is the main reaction mechanism. This is in agreement with [29] who found that the maximum direct oxidation rate can be estimated from:

$$J_L = nFDc / \delta \quad (\text{Eq. 1.1})$$

Where J_L is the mass transfer limited current density (A m⁻²), n is the number of electrons involved (i.e. 2 for the oxidation of sulfide to sulfur), F the Faraday constant (96485.3 C mol⁻¹), D the diffusion coefficient (cm² s⁻¹), c the concentration of the component in the bulk solution (mol cm⁻³ and δ the thickness of the Nernst diffusion layer (cm). Mills and Lobo found that the diffusion of sulfide species at 25°C is 1.73×10⁻⁵ cm² s⁻¹ [30]. Hence, under the conditions found in sewer systems with sulfide concentrations around 2.82×10⁻⁷ mol m⁻³ (i.e. ~10 mg L⁻¹), the direct sulfide oxidation rate is approximately 1 A m⁻². Furthermore, the batch experiments showed that at low

concentrations the sulfide oxidation rate was approximately 8 times lower compared to the continuous experiments, with an obtained sulfide oxidation rate of $3.4 \pm 1.0 \text{ mg S L}^{-1} \text{ h}^{-1}$. This is in agreement with values found in literature ($1.5\text{-}5.2 \text{ mg S L}^{-1} \text{ h}^{-1}$) for chemical sulfide oxidation with oxygen in domestic wastewater at low concentrations [3, 19, 31]. This suggests that under the applied experimental conditions, indirect oxidation of sulfide by in-situ generated oxygen is the predominant reaction mechanism, whereas direct sulfide oxidation appears negligible. Therefore, under the conditions normally found in sewer systems, Ta/Ir MMO coated titanium electrodes appear suitable for in-situ oxygen generation.

Table 3. Electron balance during sulfide oxidation from (a) synthetic feed in presence of trace elements, acetate, and chloride and (b) domestic waste water at a current density of 50 A m⁻² (n=2).

synthetic feed				domestic wastewater				
input	output		input	output				
	added	removed	produced	energy requirement	added	removed	produced	energy requirement
		(mg)	(mg)	(C)		(mg)	(mg)	(C)
HS-S (mg)	939±51	603±87			883±67	681±92		
sulfur (mg)	0		173±56	1042±337	0		110±81	665±489
S ₂ O ₃ -S (mg)	0		195±86	2347±1041	0		431±18	5203±219
SO ₃ -S (mg)	0		24±9	440±169	0		11±1	200±11
SO ₄ -S (mg)	0		211±65	5096±1560	0		125±24	3013±571
O ₂ (mg)	0		212±23	2561±283	0		78±7	946±79
organics (mg)	2085±45 ^{a)}	15±20		0	2565±5121	n.d.		
electrons (C)	10800±0			11486±270	10800±0			10027±772
electron balance				electron balance				
coulombs (C)	-686±270						773±772	
%	106±3%						93±7%	

Oxygen injection is presently considered as an attractive option for sulfide abatement in sewer systems. Oxygen can both inhibit the activity of sulfate reducing bacteria (SRB) and oxidize the sulfide that has been produced [3]. It is less expensive than most other chemicals and can target rising mains where the SRB activity is the highest [5]. Advantages of generating oxygen in-situ compared to traditional methods for oxygen supply are the fine dispersion, high controllability, the ease to monitor and no requirement for transport and storage. The disadvantage is the cost of the oxygen per unit weight; for a coulombic efficiency of 95%, a cell voltage of 5 V and a cost of \$0.06 per kWh the estimated cost is \$1.06 kg⁻¹, relative to a delivery cost of \$0.54-0.82 kg⁻¹ for standard oxygen purchases [32]. However, standard oxygen injection in sewer systems has a limited efficiency due to inefficiencies during dosing (i.e., coarse bubbles), which can result in an significant loss of undissolved gas from air in gas release valves downstream [32]. The latter is avoided when oxygen is generated in-situ due to the high transfer efficiency and fine dispersion of in-situ generated oxygen.

4.2 Final product of oxidation

We aimed to oxidise sulfide to elemental sulfur, as this reaction minimizes the electron and thus energy input [13]. Possibly formed sulfite, thiosulfate and sulfate remain in the liquid phase and can therefore be reduced again to sulfide in rising mains downstream of the electrochemical cell. In all experiments a mixture of sulfur, thiosulfate and sulfate was produced (sulfite was negligible). This means that sulfide cannot be selectively oxidized to elemental sulfur using titanium coated IrOx at high current densities. This is in contrast with the selective oxidation to sulfur observed in carbon based, low current density systems [1, 33], where no oxygen is formed and sulfide is oxidized directly at the electrode surface. However, for application in sewer systems, low current densities (and hence low anode potential) are not practical due to the large reactor size that would be required.

4.3 Influence of trace elements, organics and chloride

The presence of metals can increase the chemical sulfide oxidation significantly, even when present in trace concentrations [22]. Indeed, during the experiments with the addition of trace elements, a 37±18 % increase in sulfide removal rate was observed, whereas the acetate and chloride concentrations remained constant. The presence or

absence of chloride did not increase or decrease sulfide removal rates during the experiments. In addition to anodic sulfide oxidation and in-situ oxygen generation, organics such as acetate and chloride, which are commonly contained in wastewater, may be oxidized depending on the electrode material used and the operating conditions. These reactions are unwarranted since they increase the required energy input and possibly form methyl radicals and ethane from acetate oxidation (i.e., through the Kolbe reaction) [34, 35]. The experiments with synthetic medium showed that the acetate concentrations remained unchanged. This is because acetate oxidation requires potentials higher than the potential of oxygen evolution at Ta/Ir MMO coated titanium electrodes [20]. In the experiments using domestic wastewater, a small decrease in COD was observed. Whether there was some direct oxidation of organics or indirect oxidation with released oxygen cannot be discerned at this stage.

Similar to the acetate, during all experiments the chloride concentrations remained constant. If chlorine were formed it could react with sulfide to form sulfur and chloride. Hence, chlorine production cannot be excluded during the experiments using defined medium. However, Ta/Ir MMO coated titanium electrodes are known to have a very high catalytic effect towards oxygen. Furthermore, chloride levels found in domestic wastewater are normally relatively low (i.e. $\pm 150\text{-}200\text{ mg L}^{-1}$) and therefore it is likely that any production would be negligible [35, 36]. The presence of chloride did not increase sulfide removal rates during the experiments.

4.4 Practical implications and future research

Taking into account the slow kinetics of direct sulfide oxidation at low sulfide concentrations, direct oxidation of sulfide in sewer system presently appears not feasible at Ta/Ir MMO coated titanium electrodes. Therefore, either indirect oxidation of sulfide with in-situ generated oxygen or the prevention of sulfide build-up (i.e. prevent sulfate reduction by maintaining aerobic conditions) seem more suitable for application. One of the possible disadvantages of this strategy is the fact that the formed sulfur species can be reduced again downstream. However, this is also the case for other approaches such as conventional oxygen injection and nitrate dosing, and will be of importance when determining the position of the treatment in the sewer network. In-situ generated oxygen possesses several advantages compared to traditional methods for oxygen supply,

including a high transfer efficiency, fine dispersion, high controllability, ease of monitoring and the lack of chemicals transport and storage.

In this study, we used a current density of 50 A m^{-2} . In order to reduce investments costs, higher current densities are preferred. While direct sulfide oxidation is limited due to the diffusion of sulfide to the electrode, oxygen generation from water is less constrained. The Ta/Ir MMO coated titanium electrodes used have a high electrochemical stability and catalytic activity for oxygen evolution [37]. The expected electrode lifetime is strongly dependent on the applied current density. A Ti/IrO_x-Sb₂O₅-SnO₂ electrode containing only 10 mol% of IrO_x was predicted to have a life time over 9 years in a strong acidic solution at a current density of 1000 A m^{-2} [38]. As the current densities in the sewer based system are lower, and the solution less corrosive, lifetimes of over 10 years can be expected, unless physical erosion of the electrode occurs due to wastewater particulates.

The installation of an electrochemical system in sewer systems is subject to a number of restrictions including prevention of particle settling and accumulation and precipitation of inorganics. Whether the system cell will be placed inside the sewer pipe or as a bypass system is yet to be determined. If placed inside the sewer pipe the mesh shaped anode will be placed onto the sewer wall to prevent particle accumulation and settling. Biofilm formation on the electrode surface will not take place due to the applied anodic potentials (strong oxidizing potential). Due to the local acidifying effect at the anode, precipitates such as calcium carbonate are not expected, although this may happen at the cathode. Possible solutions are periodic chemical cleaning (i.e. acid dosage) or by switching the polarity of the electrode. To minimize ohmic losses, anodes and cathodes will need to be spaced as closely as possible; therefore a flat membrane electrode assembly (mesh structure) is proposed. Passivation of the electrode surface by sulfur during long-term continuous application is not expected since the applied current densities will result in in-situ generation of oxygen.

5. Conclusions

In this study, simultaneous sulfide oxidation and in-situ oxygen generation was demonstrated using Ta/Ir MMO coated titanium electrodes with both synthetic and real domestic wastewater at high rates. The maximum observed sulfide removal rate was $11.8 \pm 1.7 \text{ g S m}^{-2}_{\text{electrode surface}} \text{ h}^{-1}$ at sulfide concentrations $\geq 30 \text{ mg L}^{-1}$ from domestic

wastewater. The final products of oxidation were sulfur, thiosulfate, sulfate and oxygen. Under the experimental conditions the indirect oxidation of sulfide with in-situ generated oxygen appears the main reaction mechanism. Acetate and chloride concentrations remained constant, indicating that Ta/Ir MMO coated titanium electrodes are very suitable electrodes for the indirect oxidation of sulfide with in-situ generated oxygen.

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APPENDIX A

Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities

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Abstract

Hydrogen sulfide generation is the key cause of sewer pipe corrosion, one of the major issues in water infrastructure. Current abatement strategies typically involve addition of various types of chemicals to the wastewater, which incurs large operational costs. The transport, storage and application of these chemicals also constitute occupational and safety hazards. In this study, we investigated high rate electrochemical oxidation of sulfide at Ta/Ir mixed metal oxide (MMO) coated titanium electrodes as a means to remove sulfide from wastewater. Both synthetic and real wastewaters were used in the experiments. Electrochemical sulfide oxidation by means of indirect oxidation with in-situ produced oxygen appeared to be the main reaction mechanism at Ta/Ir MMO coated titanium electrodes. The maximum obtained sulfide removal rate was $11.8 \pm 1.7 \text{ g S m}^{-2} \text{ projected anode surface h}^{-1}$ using domestic wastewater at sulfide concentrations of $\geq 30 \text{ mg L}^{-1}$ or higher. The final products of the oxidation were sulfate, thiosulfate and elemental sulfur. Chloride and acetate concentrations did not entail differences in sulfide removal, nor were the latter two components affected by the electrochemical oxidation. Hence, the use of electrodes to generate oxygen in sewer systems may constitute a promising method for reagent-free removal of sulfide from wastewater.

keywords: sewer corrosion, electrochemical systems, sulfide oxidation, in-situ oxygen generation

1. Introduction

Hydrogen sulfide is ubiquitously found in domestic and industrial wastewaters [1]. It is a toxic, corrosive and odorous compound, often requiring removal from the aqueous or gaseous phase before discharge into the environment. Hydrogen sulfide is of particular concern in sewer systems since it causes corrosion of sewer pipes. Current technologies for sulfide abatement in sewer systems involve adding chemicals to wastewater to prevent sulfide formation, or its transformation from liquid to gas phase [2]. The commonly used chemicals include oxidants such as oxygen [3, 4] and nitrate [5, 6] for sulfide oxidation, iron salts for sulfide precipitation [7-9] and magnesium hydroxide to elevate pH [4, 10]. Other chemicals used include chlorine, hydrogen peroxide, caustic and nitrite, which are toxic to sewer biofilms [4, 11]. These strategies are considered expensive (\$1.7-7.2 kg S removed⁻¹) [4] and often come with a number of limitations such as sludge generation or loss of organics, the latter are needed for nutrient removal in downstream WWTPs.

Recent advances in electrode development and operation have increased the interest in electrochemical abatement strategies. Electrochemical techniques offer several advantages including no requirement for dosing, transport and storage of hazardous chemicals, robustness, versatility, controllability and the amenability to automation [12]. A typical electrochemical reactor consists of an anode, a cathode and a membrane separating both. At the anode, electrochemical oxidation of a pollutant (here sulfide) can be achieved. Electrochemical oxidation can either be achieved by direct oxidation at the electrode surface or by indirect oxidation. During indirect electrochemical oxidation, oxidants including OH[•], O₂ and Cl₂, are generated at the anode surface; these subsequently oxidize the pollutant in the bulk solution. The reaction mechanism and selectivity of the oxidation process is mainly determined by the electrode material, the flow regime and the applied anode potential. Thus, depending on the conditions, sulfide can be oxidized at the anode or oxidized by in-situ generated oxidants. Sulfide can be oxidized to elemental sulfur, thiosulfate or sulfate. The oxidation of sulfide to sulfur is preferable since this requires the least amount of electrons and thus energy input [13].

A number of studies on aqueous electrochemical sulfide oxidation have been performed in the past [1, 13-18]. However, most of these studies reported on the direct oxidation of sulfide to elemental sulfur at carbon based anode materials using high strength/conductivity solutions such as alkaline media and brine solutions, at high sulfide concentrations and predominantly operated at low current densities [13-16]. However, for sewer systems, low current densities

using high surface area carbon based electrodes are not feasible due to the large reactor size that would be required. Domestic wastewater typically has a sulfide content of around $\sim 10 \text{ mg HS}^- \text{ L}^{-1}$, which is much lower than the concentrations tested in the aforementioned studies [19]. Furthermore, since the electrochemical cell has to treat raw unfiltered sewage, flat mesh shaped electrodes are needed to avoid blockage and ragging of the system. Taking into account the low sulfide concentration and the use of flat mesh shaped electrodes (low surface area) indirect electrochemical reactions are likely to play a dominant role due to the limited reactant availability at the electrode surface.

IrOx coated titanium electrodes are extensively used as oxygen evolution electrodes in electroflotation and electrocoagulation reactors [20]. Miller and Chen reported on the direct anodic sulfide oxidation using titanium based $\text{Ti/Ta}_2\text{O}_5\text{-IrO}_2$ electrodes from a caustic medium [21]. This implies that, depending on the operational conditions (e.g. anode potential, sulfide concentrations), simultaneous sulfide oxidation and in-situ oxygen generation should be achievable. This oxygen can be used as a downstream control measure by either inhibiting the activity of sulfate reducing bacteria (SRB) and/or the oxidation of the sulfide that has been produced [3]. The kinetics and stoichiometry of the oxidation of sulfide by oxygen is well described in literature [19, 22].

Therefore, the aim of this study was to examine the feasibility of simultaneous oxidation of aqueous sulfide to elemental sulfur and water to oxygen at high current densities, using defined synthetic feed and domestic wastewater and a Ta/Ir MMO coated titanium electrode as anode.

2. Materials and Methods

2.1 Electrochemical cell and operation

The two-chambered electrochemical cell consisted of two parallel Perspex frames (internal dimensions $14 \times 12 \times 2 \text{ cm}$) separated by a cation exchange membrane (Ultrex CM17000, Membranes International Inc., USA). In the anode chamber, a mesh shaped Ta/Ir MMO ($\text{TaO}_2 / \text{IrO}_2$: 0.35/0.65) coated titanium electrode with a projected surface area of 100 cm^2 was used (Magneto Anodes BV, The Netherlands). Stainless steel fine mesh (168 cm^2) with a stainless steel current collector (6 mm mesh size, 0.8 mm wire) was used as electrode material in the cathode chamber. The anode liquid medium was constantly recirculated over an external buffer vessel, allowing a total anode liquid volume of 5 L. We operated the

reactors in fed batch mode, as a once through system would have required cubic metre volumes of defined media/sewage per day to enable operation of the reactors at the desired current densities. The latter was not practical in the laboratory. The disadvantage of this recirculatory mode, however, is that the “influent” sulfide concentration into the reactor will slowly increase if 100% removal efficiency is not achieved. In the experiments, the sulfide concentrations increased to 30 to $\sim 90 \text{ mg L}^{-1}$, depending on the current applied and anode medium used, as the experiments progressed. An example of the typical sulfide concentration profile during the course of the experiments is shown in Figure 4.

The influent flow rate through the anode chamber was maintained at 15 L h^{-1} using a peristaltic pump (Watson Marlow, UK). The off gas coming from the external buffer vessel was sent through a water-lock containing a 0.2 M NaOH solution. The recirculation flow in the anode chamber was kept at 22 L h^{-1} using a peristaltic pump (Watson Marlow, UK) to obtain a higher mixing rate in the anode chamber. PVC tubing with an internal diameter of 4.5 mm was used for the feeding and recirculation lines.

In all experiments, an Ag/AgCl (RE-5B, Bio Analytical, USA) was used as the reference electrode. Its potential was estimated at $+197 \text{ mV}$ versus standard hydrogen electrode (SHE).

An external buffer flask of 2 L was used in the recirculation of the cathode chamber. A 0.1 M NaOH solution in the cathode chamber was used in all experiments to trap any possible crossover of hydrogen sulfide. The recirculation flow of the cathode solution was kept at 22 L h^{-1} using a peristaltic pump (Watson Marlow, UK). Experiments were initially performed using a defined synthetic feed (with composition to be described later) and subsequently domestic wastewater. Both for the synthetic and real domestic wastewater experiments, sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was supplied continuously to the incoming line of the anode chamber via a syringe pump (NE-1600, New Era Pump Systems, Inc., USA) at a dosing rate of $149 \pm 20 \text{ mg S h}^{-1}$, i.e. sufficient to give an anode influent concentration of $\sim 10 \text{ mg S L}^{-1}$. Before use, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ crystals were washed with milliQ ($18 \text{ M}\Omega$) water to remove oxidized sulfur species on the surface of the crystals [1]. Due to the production of protons at the anode, a decrease of the anode pH is expected over time. To compensate for this, NaHCO_3^- was added (5 g L^{-1}) in the experiments using synthetic feed to maintain pH values commonly found in sewer systems. As the buffer capacity of domestic wastewater was not sufficient the pH was maintained at 7.5 by a PLC controlled dosage of a 0.5 M NaOH solution. The latter is not required in a practical situation since there a once through system would be implemented. An overview of the experimental setup is presented in Figure 1.

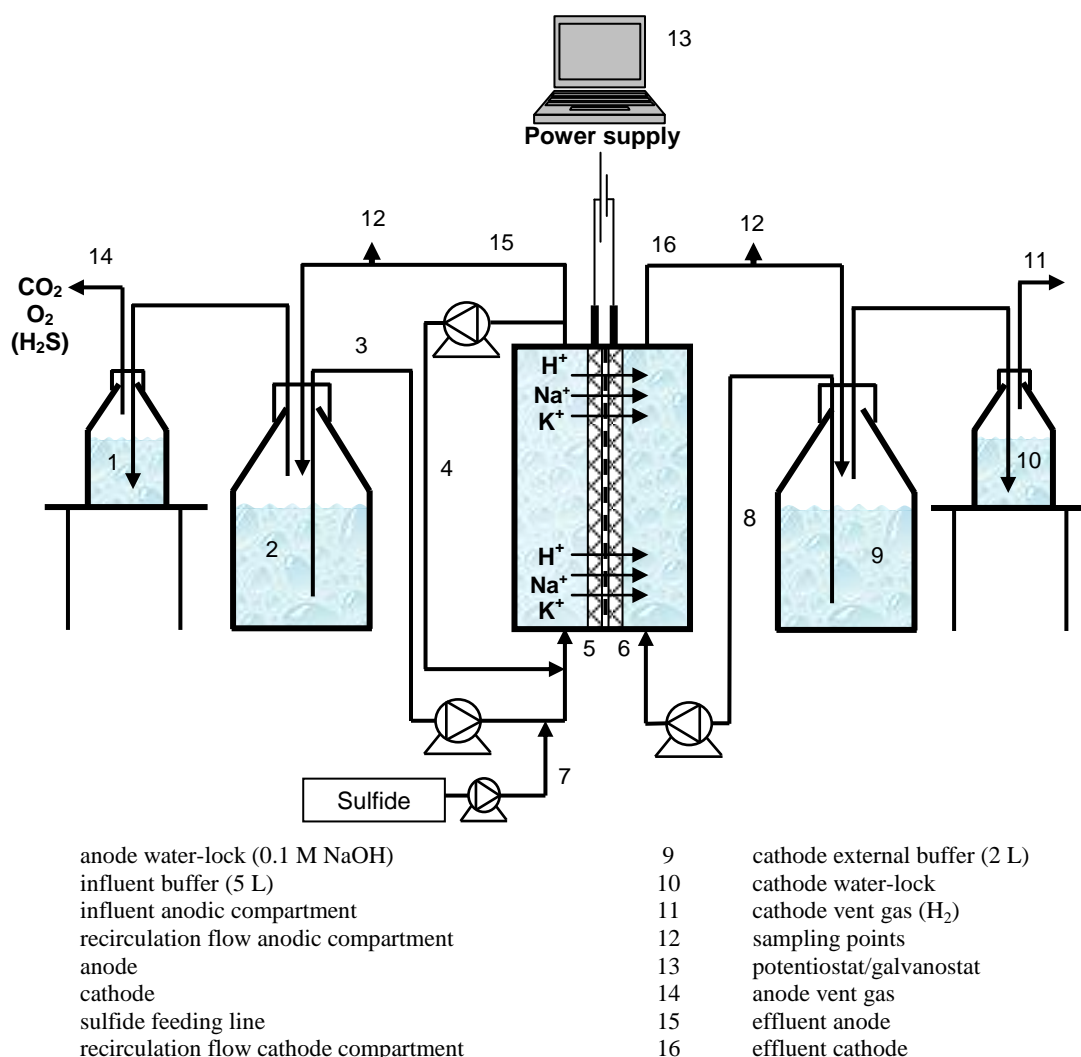


Fig. 1. Schematic overview experimental setup

2.2 Measurements and calculations

Galvanostatic measurements and controls were performed using a Wenking potentiostat/galvanostat (KP07, Bank Elektronik GmbH, Germany). The anode potentials and the current were recorded every 60 seconds using an Agilent 34970A data acquisition unit. All calculations were performed according to Logan et al and Rabaey et al [23, 24]. Coulombic efficiencies were determined on the basis of sulfide to elemental sulfur conversion.

2.3 Experimental procedures

Experiments, divided into 4 different sets, were conducted to verify the feasibility of electrochemical sulfide oxidation at high current density from synthetic and real domestic wastewater. Each time, the performance was assessed in 6 hour experimental runs using

galvanostatic control at different current densities. During the experiments with continuous sulfide dosing, sulfide was fed at a rate of $149 \pm 20 \text{ mg S h}^{-1}$ to the reactor during six hours. This is equivalent to a loading rate of $444 \pm 60 \text{ mg S L}^{-1}_{\text{anode volume}} \text{ h}^{-1}$, or a current (density) of $\sim 250 \text{ mA}$ (25 A m^{-2}) (i.e., based on a 2-electron oxidation of sulfide to elemental sulfur). Prior to every run, the Ta/Ir MMO coated titanium electrode was rinsed in an alkaline sodium sulfide solution to remove deposited elemental sulfur (i.e. formation of soluble polysulfides) and subsequently rinsed with miliQ ($18 \text{ M}\Omega$) water to remove any aqueous (poly)sulfides left in the electrochemical cell. Aqueous sulfur species (i.e. sulfide, sulfite, thiosulfate and sulfate), acetate and COD concentrations were measured in 1.5 hours intervals during the continuous experiments and every 1 hour during the batch experiments. IC analysis of the anode water-lock was performed at the end of every experiment to account for the amount of any H_2S stripped from the buffer vessel.

IC analysis of the cathode compartment was performed during initial experiments to determine possible transfer of H_2S gas from the anode to the cathode through the membrane. These results indicated negligible transfer of H_2S from anode to cathode, which is in agreement with [1] and with what would be expected from a cation exchange membrane (as sulfide is an anion). Therefore, in the experiments from thereon it was assumed that no transfer of H_2S through the membrane occurred.

2.3.1 Experiment 1

In the first set of experiments synthetic feed was used to determine the impact of current density on the kinetics on the sulfide oxidation process and the final products of sulfide oxidation. Experiments were performed in triplicate at fixed current densities of 25, 50 and 100 A m^{-2} , respectively.

2.3.2 Experiment 2

In the second set of experiments, synthetic feed was used to investigate the impact of the presence of alternative electron donors (i.e. acetate) and chloride. Furthermore, trace elements in concentrations normally found in domestic wastewater, were added to investigate their catalytic effect (i.e. catalysts for auto-oxidation of sulfide) on chemical sulfide oxidation with in-situ oxygen generation. Trace elements composition and concentrations normally found in domestic wastewater were used according to Rabaey *et al.* [25]. Two different experiments were performed: (a) sulfide oxidation in presence of trace elements and the

absence of both acetate and chloride (in triplicate), (b) sulfide oxidation in the presence of acetate ($424 \pm 8 \text{ mg L}^{-1}$), chloride ($170 \pm 5 \text{ mg L}^{-1}$) and trace elements (in quintuplicate). Experiment (a) was performed at a fixed current density of 50 A m^{-2} to investigate their catalytic effect on chemical sulfide oxidation with in-situ oxygen generation whereas experiment (b) was performed to investigate if organics (e.g. acetate) and/or chloride (i.e. in-situ production of chlorine) are electrochemically oxidized during sulfide oxidation.

2.3.3 Experiment 3

The third set of experiments was performed (in quintuplicate) at a fixed current density of 50 A m^{-2} to determine the kinetics, coulombic efficiency and reaction products of sulfide oxidation in domestic wastewater.

2.3.4 Experiment 4

The fourth set of experiments was performed to investigate the oxidation kinetics of sulfide at concentrations close to 1 mg L^{-1} (i.e. target concentration in sewer systems). Therefore, batch tests were performed (in triplicate) using domestic wastewater at a fixed current density of 50 A m^{-2} spiked with sulfide to obtain an initial concentration of ($8.3 \pm 0.75 \text{ mg L}^{-1}$).

2.4 Chemical analyses

Sulfide, sulfite, thiosulfate and sulfate concentrations were measured with Ion Chromatography (IC), using the Dionex 2010i system, according to Keller-Lehman *et al.* (2006) [26]. Samples collected from the reactors were immediately filtered by a $0.22 \text{ }\mu\text{m}$ syringe filter (Millipore, USA) and preserved in previously prepared Sulfide Antioxidant Buffer (SAOB) solution prior to ion chromatography analysis. SAOB solution was also used to dilute the samples when necessary. SAOB solution was prepared using nitrogen purged MilliQ ($18 \text{ M}\Omega$) water, 3.2 g L^{-1} NaOH and 2.8 g L^{-1} α -ascorbic acid. After preparation, the solution was kept refrigerated, shielded from light and not used beyond 24 hours.

Sulfide concentrations were also measured with a handheld ion selective electrode for sulfide measurements (Sentek, Sentek Type 3225, United Kingdom). Samples from the reactor were immediately filtered by a $0.22 \text{ }\mu\text{m}$ syringe filter (Millipore, USA) and preserved in previously prepared Sulfide Antioxidant Buffer (SAOB) to obtain a SAOB to sample ratio of 1:1. SAOB solution was prepared using nitrogen purged MilliQ ($18 \text{ M}\Omega$) water, 80 g L^{-1}

NaOH, 67 g L⁻¹ EDTA and 35 g L⁻¹ α-ascorbic acid (as recommended by supplier). Calibration curves were obtained by combining the sulfide concentrations from IC analysis with the observed redox potentials using the ion selective electrode. In this way, possible drift of the electrode is ruled out since the electrode is internally calibrated every time an analysis is performed.

COD concentrations were determined by means of COD cuvette tests (Merck, range 25-1500 mg L⁻¹). Volatile fatty acids (VFAs) concentration was determined by High Performance Liquid Chromatography (HPLC). The pH was either controlled online or measured using a hand-held meter (Cyberscan PC 300, Eutech Instruments).

Produced gas was collected in gas collection bags (SKC Tedlar 1 Liter Sample Bag). The collected gas was analysed for O₂ concentrations using a gas chromatograph (Shimadzu, molecular sieve, stainless steel, 6 ft × 1 × 8" OD).

3. Results

3.1 Sulfide oxidation from synthetic feed in the absence of trace elements, chloride and acetate

The results of the experiments from synthetic feed at current densities of 25, 50 and 100 A m⁻² are detailed in Table 1. The sulfide removal rates increased from 6.1±0.3 to 9.2±0.4 g S m⁻² anode surface h⁻¹ when the current density was increased from 25 to 100 A m⁻². Figure 2A shows the total amount of sulfide removed (mg S) at the applied current densities. Increasing the current density from 50 to 100 A m⁻² did not result in significantly higher sulfide removal rates. However, it did result in higher gas production, indicating more oxygen was produced in-situ.

The pH at the start of all experiments using synthetic wastewater was 8.3. As oxidation progressed, the pH decreased to ~7 due to the release of protons generated as the sulfide is removed from the solution. The observed in-situ gas production (i.e. oxygen) at current densities of 25, 50 and 100 A m⁻² were 319±1, 808±29 and 1843±64 mL, respectively, which is higher than the maximum attainable oxygen (i.e., 343.75, 687.5 and 1375 mL) if all electrons are used for oxygen generation. Analysis of the gas composition performed in the second set of experiments confirmed that the extra gas produced originated from stripping of CO₂. Over the course of the experiments the anode potentials remained fairly constant.

Table 1. Sulfide oxidation from synthetic feed at current densities of 25, 50 and 100 A m⁻² using a NaHCO₃⁻ buffer solution

parameter	unit	value		
current density	A m ⁻²	25	50	100
coulombic efficiency	%	44±3	30±5.5	14.3±0.8
removal rate	mg S h ⁻¹	63.5±5	80.7±11	98.9±10
	mg S m ⁻² anode surface h ⁻¹	6.06±0.25	8.13±1.26	9.16±0.37
SO ₃ -S produced	%	6.4±3.0%	3.5±1.6%	2.4±0.7%
S ₂ O ₃ -S produced	%	25.8±6.9%	21.3±3.6%	9.8±0.6%
SO ₄ -S produced	%	36.1±7.7%	36.1±3.5%	27.1±2.9%
S ⁰ produced ^{a)}	%	29.3±17.2%,	38.3±5.3%	53.6±1.3%
gas production	mL	319±1	808±29	1843±64

a) The difference in sulfide-S added and sulfide-S removed (i.e., oxidized to SO₃-S, S₂O₃-S and SO₄-S) was assumed to be elemental sulfur present in solid form or in soluble form as polysulfide.

3.2 Sulfide oxidation from synthetic feed in presence of (a) trace elements and (b) trace elements, acetate and chloride

The results of the experiments from synthetic feed at a current density of 50 A m⁻² in the presence of trace elements, chloride and acetate are detailed in Table 2. The average obtained sulfide removal rate was 10.9±0.6 in the presence of trace elements and 11.2±1.6 g S m⁻² anode surface h⁻¹ in the presence of trace elements, chloride and acetate, respectively. This was 34±13% and 37±18% higher than the removal rate obtained with synthetic feed without (a) trace elements and (b) acetate, chloride and trace elements. Figure 2B shows the total amount of sulfide removed (mg S) in the presence of (a) trace elements and (b) trace elements, acetate and chloride at a fixed current density of 50 A m⁻².

Acetate analysis confirmed that acetate was not significantly removed (i.e., 1.9±3.0%). The presence or absence of chloride did not result in either an increase or decrease in obtained sulfide removal rate. Analysis of the gas composition showed that 35.4±1.2 mg hr⁻¹ of excess oxygen was generated. In Table 3 a summary of the electron balance is presented.

Table 2. Sulfide oxidation from synthetic feed in (a) absence of trace elements, acetate and chloride, in presence of (b) trace elements and (c) trace elements, acetate, and chloride and (d) domestic waste water at a current density of 50 A m⁻²

parameter	unit	HCO ₃ ⁻ buffer solution	trace elements	trace elements, acetate and chloride	domestic waste water
coulombic efficiency	%	30±5.5	32%±1	33%±2	40%±2
removal rate	mg S h ⁻¹	80.7±11	123.5±0.6	129±12	136±18
	mg S m ⁻² anode surface h ⁻¹	8.13±1.26	10.86±0.6	11.38±1.15	11.76±1.68
SO ₃ -S produced	%	3.5±1.6%	4.1±1.1	2.8±1.3	2.1±0.9
S ₂ O ₃ -S produced	%	21.3±3.6%	32.4±0.6	34.4±4.9	62.4±11.1
SO ₄ -S produced	%	36.1±3.5%	26.1±1.2	28.8±5.2	13.9±4.6
S ⁰ produced ^{a)}	%	38.3±5.3%	37.0±1.7	44±22	21.6±14.4
acetate removal	%	n.d.	n.d.	1.9±3	9±4
gas production	mL	808±29	800±70	750±4	283±5
oxygen produced	mg	not measured	not measured	212±7 ^{b)}	76±6 ^{b)}

^{a)} The difference in sulfide-S added and sulfide-S removed (i.e., oxidized to SO₃-S, S₂O₃-S and SO₄-S) was assumed to be elemental sulfur present in solid form or in soluble form as polysulfide.

^{b)} Measured in duplicate.

3.3 Sulfide oxidation from domestic wastewater

The results of the experiments from domestic waste water at a current density of 50 A m^{-2} are detailed in Table 2. The average obtained sulfide removal rate was in the same order as the removal rates obtained from synthetic feed in the presence of trace elements (i.e. 11.8 ± 1.7 versus 10.9 ± 0.6 and $11.2 \pm 1.6 \text{ g S m}^{-2} \text{ anode surface h}^{-1}$). Analysis of the gas composition showed that $13 \pm 1 \text{ mg hr}^{-1}$ of oxygen was produced. COD analyses revealed that the average COD removal was $9 \pm 4\%$. During the experiments the anode potentials remained fairly constant at $3.4 \pm 0.4 \text{ Volt}$. In Table 3 a summary of the electron balance is presented.

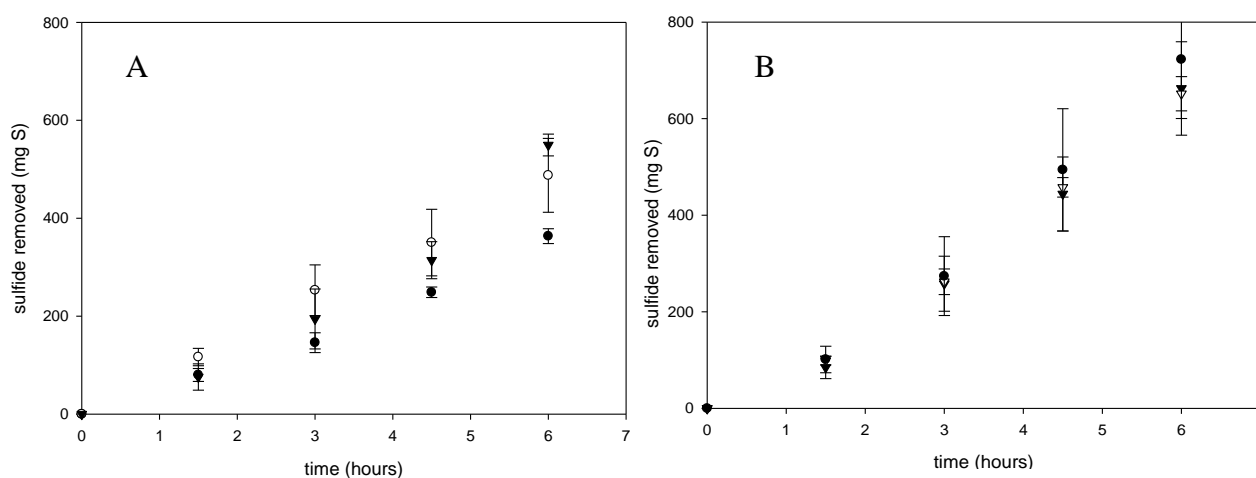


Fig. 2A. Comparisons of the amount of sulfide removed (mg S) in the absence of trace elements, acetate and chloride at fixed current densities of 25, 50, 100 A m^{-2} ($n=3$): (●) 25 A m^{-2} , (○) 50 A m^{-2} and (▼) 100 A m^{-2} . **Fig. 2B.** Comparisons of the amount of sulfide removed (mg S) in the presence of (▽) trace elements ($n=3$), (▼) trace elements, acetate and chloride ($n=5$) and (●) domestic wastewater ($n=5$) at a fixed current density of 50 A m^{-2} .

3.4 Batch test for sulfide oxidation at low concentrations

The results of the batch tests for sulfide oxidation at low concentrations at a fixed current density of 50 A m^{-2} are shown in Figure 3. The average sulfide removal rate was $16.8 \pm 5.0 \text{ mg S h}^{-1}$, which is equal to a removal rate of $1.7 \pm 0.5 \text{ g S m}^{-2} \text{ anode surface h}^{-1}$, approximately one eighth of the removal rates obtained during the continuous experiments.

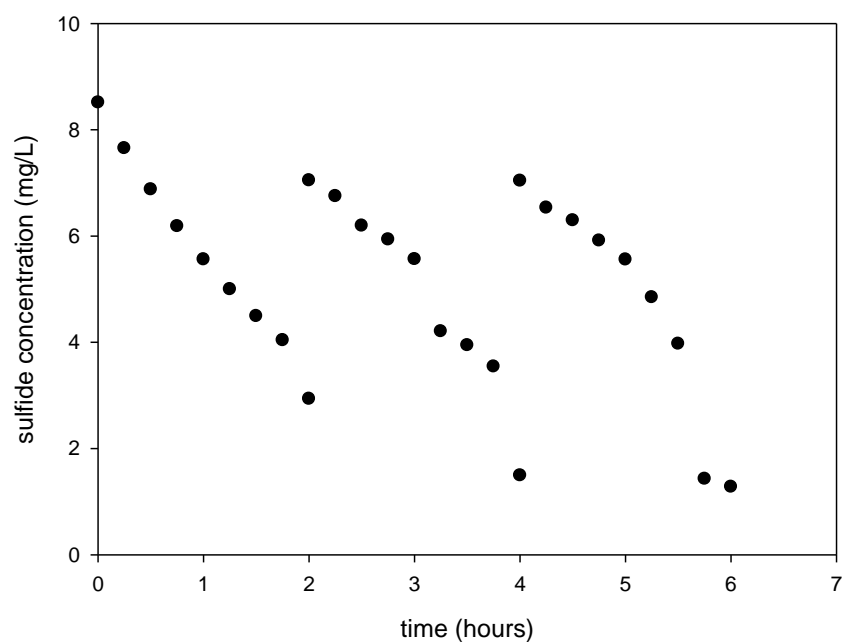


Figure 3. Sulfide concentration (mg L^{-1}) profile using at a current density of 50 A m^{-2} using domestic wastewater spiked with sulfide.

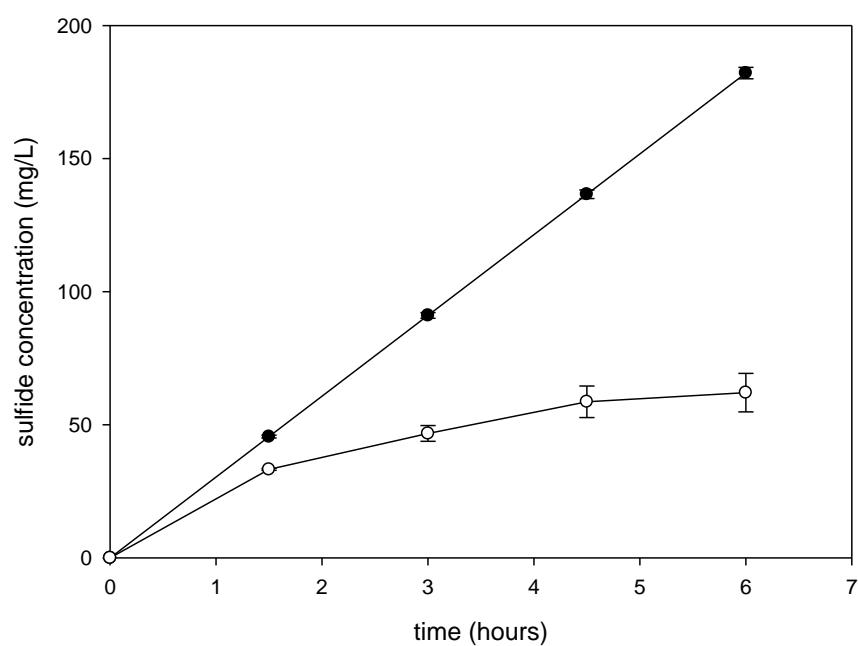


Figure 4. Typical sulfide generation profile during galvanostatic control at a current density of 50 A m^{-2} in the presence of acetate, chloride and trace elements ($n=3$): (●) sulfide dosed (mg L^{-1}) and ○ sulfide concentration.

4. Discussion

4.1 Sulfide oxidation and in-situ oxygen generation

In this work, we investigated the simultaneous aqueous sulfide oxidation and in-situ oxygen generation using Ta/Ir MMO coated titanium electrodes. The impact of organics (i.e. acetate), chloride and trace elements on the kinetics on sulfide oxidation and in-situ oxygen generation was successfully investigated.

To investigate the kinetics of sulfide oxidation at low concentrations, batch experiments with low sulfide concentrations were performed as well. Aqueous sulfide removal by electrochemical oxidation with concomitant in-situ oxygen generation was demonstrated using defined synthetic media as well as domestic wastewater.

Increasing the applied current from 50 to 100 A m⁻² did not proportionally enhance sulfide oxidation, hence the coulombic efficiency decreased. The higher current caused more diversion of the electrons towards gas production (oxygen), which in a practical situation can be used for downstream sulfide control (i.e., prevention of sulfate reduction) or aqueous phase based sulfide oxidation [3, 27]. The expected sulfide oxidation rate (mg S L⁻¹ h⁻¹) from domestic wastewater with pure oxygen at a sulfide concentration of 30 mg L⁻¹ and a dissolved oxygen concentration of 40 mg L⁻¹ would be 28.7 mg S L⁻¹ h⁻¹ [28]. The observed sulfide removal rate in the experiments using domestic wastewater was 23.5±3.0 mg S L⁻¹ h⁻¹, indicating indirect oxidation of sulfide with in-situ generated oxygen is the main reaction mechanism. This is in agreement with [29] who found that the maximum direct oxidation rate can be estimated from:

$$J_L = nFDc / \delta \quad (\text{Eq. 1.1})$$

Where J_L is the mass transfer limited current density (A m⁻²), n is the number of electrons involved (i.e. 2 for the oxidation of sulfide to sulfur), F the Faraday constant (96485.3 C mol⁻¹), D the diffusion coefficient (cm² s⁻¹), c the concentration of the component in the bulk solution (mol cm⁻³ and δ the thickness of the Nernst diffusion layer (cm). Mills and Lobo found that the diffusion of sulfide species at 25°C is 1.73×10⁻⁵ cm² s⁻¹ [30]. Hence, under the conditions found in sewer systems with sulfide concentrations around 2.82×10⁻⁷ mol m⁻³ (i.e. ~10 mg L⁻¹), the direct sulfide oxidation rate is approximately 1 A m⁻². Furthermore, the batch experiments showed that at low

concentrations the sulfide oxidation rate was approximately 8 times lower compared to the continuous experiments, with an obtained sulfide oxidation rate of $3.4 \pm 1.0 \text{ mg S L}^{-1} \text{ h}^{-1}$. This is in agreement with values found in literature ($1.5\text{-}5.2 \text{ mg S L}^{-1} \text{ h}^{-1}$) for chemical sulfide oxidation with oxygen in domestic wastewater at low concentrations [3, 19, 31]. This suggests that under the applied experimental conditions, indirect oxidation of sulfide by in-situ generated oxygen is the predominant reaction mechanism, whereas direct sulfide oxidation appears negligible. Therefore, under the conditions normally found in sewer systems, Ta/Ir MMO coated titanium electrodes appear suitable for in-situ oxygen generation.

Table 3. Electron balance during sulfide oxidation from (a) synthetic feed in presence of trace elements, acetate, and chloride and (b) domestic waste water at a current density of 50 A m⁻² (n=2).

synthetic feed				domestic wastewater				
input	output		input	output				
	added	removed	produced	energy requirement	added	removed	produced	energy requirement
		(mg)	(mg)	(C)		(mg)	(mg)	(C)
HS-S (mg)	939±51	603±87			883±67	681±92		
sulfur (mg)	0		173±56	1042±337	0		110±81	665±489
S ₂ O ₃ -S (mg)	0		195±86	2347±1041	0		431±18	5203±219
SO ₃ -S (mg)	0		24±9	440±169	0		11±1	200±11
SO ₄ -S (mg)	0		211±65	5096±1560	0		125±24	3013±571
O ₂ (mg)	0		212±23	2561±283	0		78±7	946±79
organics (mg)	2085±45 ^{a)}	15±20		0	2565±5121	n.d.		
electrons (C)	10800±0			11486±270	10800±0			10027±772
electron balance				electron balance				
coulombs (C)	-686±270						773±772	
%	106±3%						93±7%	

Oxygen injection is presently considered as an attractive option for sulfide abatement in sewer systems. Oxygen can both inhibit the activity of sulfate reducing bacteria (SRB) and oxidize the sulfide that has been produced [3]. It is less expensive than most other chemicals and can target rising mains where the SRB activity is the highest [5]. Advantages of generating oxygen in-situ compared to traditional methods for oxygen supply are the fine dispersion, high controllability, the ease to monitor and no requirement for transport and storage. The disadvantage is the cost of the oxygen per unit weight; for a coulombic efficiency of 95%, a cell voltage of 5 V and a cost of \$0.06 per kWh the estimated cost is \$1.06 kg⁻¹, relative to a delivery cost of \$0.54-0.82 kg⁻¹ for standard oxygen purchases [32]. However, standard oxygen injection in sewer systems has a limited efficiency due to inefficiencies during dosing (i.e., coarse bubbles), which can result in an significant loss of undissolved gas from air in gas release valves downstream [32]. The latter is avoided when oxygen is generated in-situ due to the high transfer efficiency and fine dispersion of in-situ generated oxygen.

4.2 Final product of oxidation

We aimed to oxidise sulfide to elemental sulfur, as this reaction minimizes the electron and thus energy input [13]. Possibly formed sulfite, thiosulfate and sulfate remain in the liquid phase and can therefore be reduced again to sulfide in rising mains downstream of the electrochemical cell. In all experiments a mixture of sulfur, thiosulfate and sulfate was produced (sulfite was negligible). This means that sulfide cannot be selectively oxidized to elemental sulfur using titanium coated IrOx at high current densities. This is in contrast with the selective oxidation to sulfur observed in carbon based, low current density systems [1, 33], where no oxygen is formed and sulfide is oxidized directly at the electrode surface. However, for application in sewer systems, low current densities (and hence low anode potential) are not practical due to the large reactor size that would be required.

4.3 Influence of trace elements, organics and chloride

The presence of metals can increase the chemical sulfide oxidation significantly, even when present in trace concentrations [22]. Indeed, during the experiments with the addition of trace elements, a 37±18 % increase in sulfide removal rate was observed, whereas the acetate and chloride concentrations remained constant. The presence or

absence of chloride did not increase or decrease sulfide removal rates during the experiments. In addition to anodic sulfide oxidation and in-situ oxygen generation, organics such as acetate and chloride, which are commonly contained in wastewater, may be oxidized depending on the electrode material used and the operating conditions. These reactions are unwarranted since they increase the required energy input and possibly form methyl radicals and ethane from acetate oxidation (i.e., through the Kolbe reaction) [34, 35]. The experiments with synthetic medium showed that the acetate concentrations remained unchanged. This is because acetate oxidation requires potentials higher than the potential of oxygen evolution at Ta/Ir MMO coated titanium electrodes [20]. In the experiments using domestic wastewater, a small decrease in COD was observed. Whether there was some direct oxidation of organics or indirect oxidation with released oxygen cannot be discerned at this stage.

Similar to the acetate, during all experiments the chloride concentrations remained constant. If chlorine were formed it could react with sulfide to form sulfur and chloride. Hence, chlorine production cannot be excluded during the experiments using defined medium. However, Ta/Ir MMO coated titanium electrodes are known to have a very high catalytic effect towards oxygen. Furthermore, chloride levels found in domestic wastewater are normally relatively low (i.e. $\pm 150\text{-}200\text{ mg L}^{-1}$) and therefore it is likely that any production would be negligible [35, 36]. The presence of chloride did not increase sulfide removal rates during the experiments.

4.4 Practical implications and future research

Taking into account the slow kinetics of direct sulfide oxidation at low sulfide concentrations, direct oxidation of sulfide in sewer system presently appears not feasible at Ta/Ir MMO coated titanium electrodes. Therefore, either indirect oxidation of sulfide with in-situ generated oxygen or the prevention of sulfide build-up (i.e. prevent sulfate reduction by maintaining aerobic conditions) seem more suitable for application. One of the possible disadvantages of this strategy is the fact that the formed sulfur species can be reduced again downstream. However, this is also the case for other approaches such as conventional oxygen injection and nitrate dosing, and will be of importance when determining the position of the treatment in the sewer network. In-situ generated oxygen possesses several advantages compared to traditional methods for oxygen supply,

including a high transfer efficiency, fine dispersion, high controllability, ease of monitoring and the lack of chemicals transport and storage.

In this study, we used a current density of 50 A m^{-2} . In order to reduce investments costs, higher current densities are preferred. While direct sulfide oxidation is limited due to the diffusion of sulfide to the electrode, oxygen generation from water is less constrained. The Ta/Ir MMO coated titanium electrodes used have a high electrochemical stability and catalytic activity for oxygen evolution [37]. The expected electrode lifetime is strongly dependent on the applied current density. A Ti/IrO_x-Sb₂O₅-SnO₂ electrode containing only 10 mol% of IrO_x was predicted to have a life time over 9 years in a strong acidic solution at a current density of 1000 A m^{-2} [38]. As the current densities in the sewer based system are lower, and the solution less corrosive, lifetimes of over 10 years can be expected, unless physical erosion of the electrode occurs due to wastewater particulates.

The installation of an electrochemical system in sewer systems is subject to a number of restrictions including prevention of particle settling and accumulation and precipitation of inorganics. Whether the system cell will be placed inside the sewer pipe or as a bypass system is yet to be determined. If placed inside the sewer pipe the mesh shaped anode will be placed onto the sewer wall to prevent particle accumulation and settling. Biofilm formation on the electrode surface will not take place due to the applied anodic potentials (strong oxidizing potential). Due to the local acidifying effect at the anode, precipitates such as calcium carbonate are not expected, although this may happen at the cathode. Possible solutions are periodic chemical cleaning (i.e. acid dosage) or by switching the polarity of the electrode. To minimize ohmic losses, anodes and cathodes will need to be spaced as closely as possible; therefore a flat membrane electrode assembly (mesh structure) is proposed. Passivation of the electrode surface by sulfur during long-term continuous application is not expected since the applied current densities will result in in-situ generation of oxygen.

5. Conclusions

In this study, simultaneous sulfide oxidation and in-situ oxygen generation was demonstrated using Ta/Ir MMO coated titanium electrodes with both synthetic and real domestic wastewater at high rates. The maximum observed sulfide removal rate was $11.8 \pm 1.7 \text{ g S m}^{-2}_{\text{electrode surface}} \text{ h}^{-1}$ at sulfide concentrations $\geq 30 \text{ mg L}^{-1}$ from domestic

wastewater. The final products of oxidation were sulfur, thiosulfate, sulfate and oxygen. Under the experimental conditions the indirect oxidation of sulfide with in-situ generated oxygen appears the main reaction mechanism. Acetate and chloride concentrations remained constant, indicating that Ta/Ir MMO coated titanium electrodes are very suitable electrodes for the indirect oxidation of sulfide with in-situ generated oxygen.

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APPENDIX B

Electrochemical sulfide oxidation from domestic wastewater using mixed metal coated titanium electrodes

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Water Research, accepted manuscript

Abstract

Hydrogen sulfide generation is a major issue in sewer management. A novel method based on electrochemical sulfide oxidation was recently shown to be highly effective for sulfide removal from synthetic and real sewage. Here, we compare the performance of five different mixed metal oxide (MMO) coated titanium electrode materials for the electrochemical removal of sulfide from domestic wastewater. All electrode materials performed similarly in terms of sulfide removal, removing $78\pm5\%$, $77\pm1\%$, $85\pm4\%$, $84\pm1\%$, and $83\pm2\%$ at a current density of 10 mA cm^{-2} using Ta/Ir, Ru/Ir, Pt/Ir, SnO_2 and PbO_2 , respectively. Elevated chloride concentrations, often observed in coastal areas, did not entail any significant difference in performance. Independent of the electrode material used, sulfide oxidation by in-situ generated oxygen was the predominant reaction mechanism. Passivation of the electrode surface by deposition of elemental sulfur did not occur. However, scaling was observed in the cathode compartment. This study shows that all the MMO coated titanium electrode materials studied are suitable anodic materials for sulfide removal from wastewater. Ta/Ir and Pt/Ir coated titanium electrodes seem the most suitable electrodes since they possess the lowest overpotential for oxygen evolution, are stable at low chloride concentration and are already used in full scale applications.

keywords: electrochemical oxidation, oxygen generation, sulfide oxidation, sewer

1. Introduction

Hydrogen sulfide is ubiquitously present in industrial and domestic waste streams, and is of special concern in sewer systems since it is responsible for odour issues in urban areas, is toxic to sewer workers, and is the main cause for sewer pipe corrosion [1]. Repair and/or replacement of corroded sewer pipes results in considerable costs [2-4], and therefore measures for mitigating sulfide production and emission are required. Current strategies to prevent sewer corrosion come with substantial costs due to both chemical consumption and system maintenance [1, 5].

Recently, we described the electrochemical oxidation of aqueous sulfide using Ta/Ir coated titanium electrodes from domestic wastewater [6]. At the used current densities of 5 mA cm⁻² sulfide could be oxidized, producing elemental sulfur, thiosulfate and sulfate as the final products. Indirect oxidation of sulfide with in-situ generated oxygen rather than the direct oxidation of sulfide at the electrode was shown to be the predominant reaction mechanism due to the low sulfide concentrations (i.e. ~10 mg L⁻¹) normally observed in sewers. In comparison to sulfide control with conventional oxygen injection, the method does not require any transport and storage of oxygen, whereas in-situ generated oxygen is expected to have a much higher efficiency due to the fine dispersion (i.e. 1-30 µm) of the generated oxygen [7].

Electrode materials possess different selectivity and catalytic activities, and may hence produce different intermediates such as oxygen, chlorine/hypochlorous acid, hydroxyl radicals and other reactive oxygen species [7]. These intermediates may have a different product spectrum for sulfide oxidation, and may increase/decrease overall oxidation efficiency. In this study, the feasibility of anodic sulfide oxidation in domestic wastewater using titanium electrodes coated with 5 different types of electrocatalyst materials, namely Ta/Ir, Pt/Ir, Ru/Ir, PbO₂ and SnO₂, was investigated.

Ta/Ir coated titanium electrodes are known for their low overpotential for oxygen and their stability. They are therefore commonly used as oxygen evolving electrodes [7]. Ru/Ir electrodes find widespread use in the chloro-alkali industry for the in-situ oxidation of chloride to chlorine/hypochlorite [8, 9]. Both Ru/Ir and Pt/Ir electrodes also possess a low overpotential for oxygen evolution, and therefore especially at low chloride concentrations oxygen evolution may become a predominant reaction mechanism. It is important to note that these electrodes have a low overpotential for the production of chlorine from chloride. In coastal areas (e.g., Queensland, Australia) the chloride concentrations in domestic wastewater

can be as high as $> 1\text{ g L}^{-1}$ due to marine infiltrations into the sewer system [10]. Hence, in-situ generation of hypochlorous acid/hypochlorite may become an important reaction mechanism for sulfide oxidation from domestic wastewater. Hypochlorous acid/hypochlorite can oxidize sulfide to elemental sulfur at $\text{pH} \leq 7.5$, values normally observed in sewer systems. Disadvantage of in-situ chlorine generation is the possible formation of toxic organochlorine derivatives [11], which needs to be prevented.

Contrarily to the three aforementioned materials, PbO_2 and SnO_2 have a high overpotential for oxygen evolution. Just like boron doped diamond (BDD), the electrocatalysts PbO_2 and SnO_2 are known to generate hydroxyl radicals from the oxidation of water [12-14]. However, contrarily to BDD, PbO_2 and SnO_2 are made of inexpensive materials which are readily available in practical mesh geometries and at scale, and have a low electrical resistivity. This makes them suitable materials for applications on large scale (i.e. industrial applications and sewer systems).

Considering the above, the main aims of this study are to assess the impact of electrode coating on electrochemical sulfide oxidation in wastewater, to assess the differences in energy requirement for the different electrode materials and to assess the impact of chloride concentrations on the sulfide oxidation process.

2. Materials and Methods

2.1 Electrochemical cell and operation

Figure 1 gives a schematic diagram of the electrochemical cell. The two-chambered electrochemical cell consisted of two parallel Perspex frames (internal dimensions $20 \times 4.8 \times 1.2$ cm) separated by a cation exchange membrane (Ultrex CM17000, Membranes International Inc., USA) to create an anode and cathode compartment each with a volume of about 100 mL. In the anode chamber, mesh shaped Ta/Ir ($\text{TaO}_2/\text{IrO}_2$: 0.35/0.65), Ru/Ir ($\text{RuO}_2/\text{IrO}_2$: 0.70/0.30), Pt/Ir ($\text{PtO}_2/\text{IrO}_2$: 0.70/0.30), PbO_2 and SnO_2 coated titanium electrodes (diameter: 240 mm; thickness: 1 mm; specific surface area: $1.0\text{ cm}^2\text{ cm}^{-2}$) were used (Magneto Anodes BV, The Netherlands). Stainless steel fine mesh (24 cm^2) with a stainless steel current collector (6 mm mesh size, 0.8 mm wire connected via a 6 mm stainless steel rod) was used as electrode material in the cathode chamber. Both the anode and cathode had a projected electrode surface area of 24 cm^2 . In all experiments, an Ag/AgCl (RE-5B, Bio Analytical, USA) was used as the reference electrode (+197 mV versus SHE).

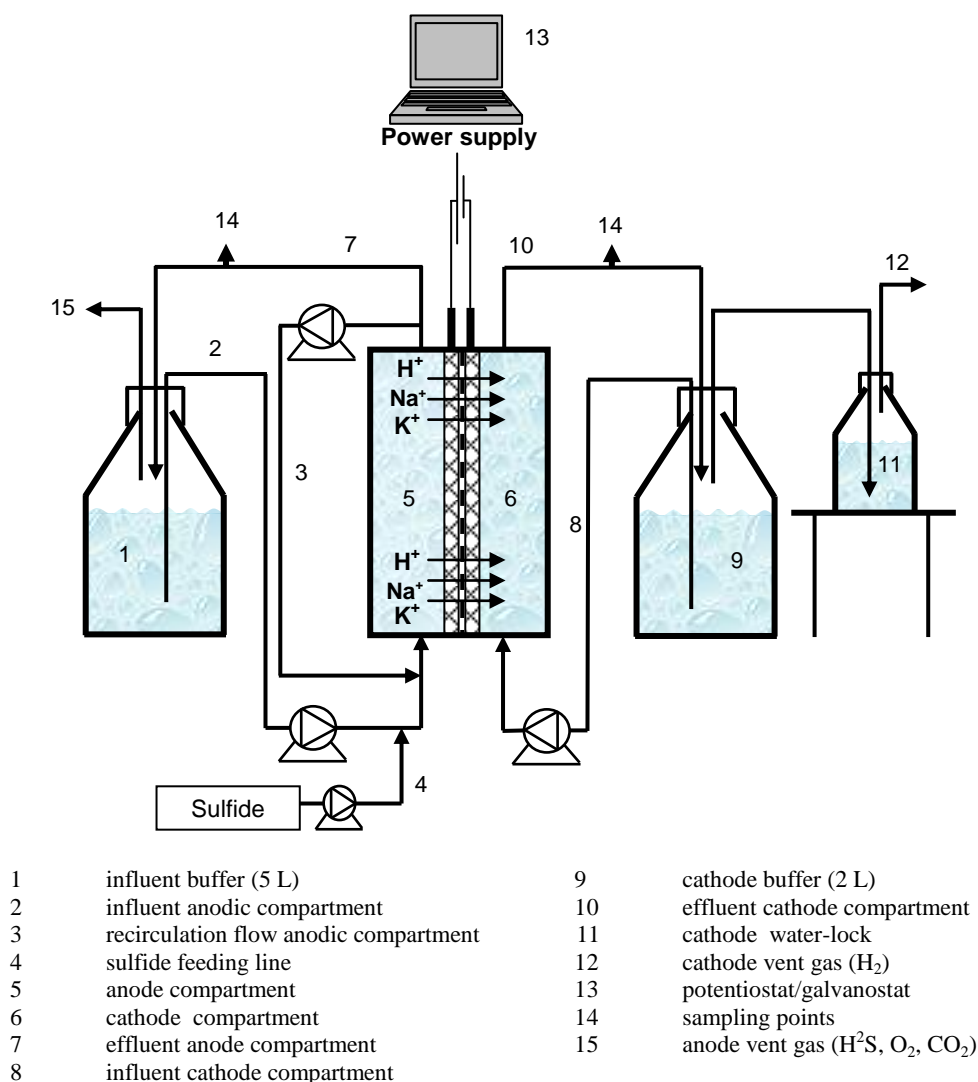


Fig. 1. Schematic overview experimental setup

The anode liquid medium was constantly recirculated over a 5 L vessel, allowing a total anode liquid volume of 5 L. The influent flow rate through the anode chamber was maintained at 3.6 L h⁻¹ using a peristaltic pump (Watson Marlow, UK). An additional recirculation flow in the anode chamber, which was kept at 22 L h⁻¹ using a peristaltic pump (Watson Marlow, UK), to obtain a good mixing rate in the anode chamber was used. PVC tubing with an internal diameter of 8 mm was used for the feeding and recirculation lines. The off-gas coming from the external buffer vessel was captured in a gas collection bag (TKC Tedlar bags, Air-Met Scientific Pty Ltd, USA).

An external buffer flask of 2 L was used in the recirculation of the cathode chamber. A 0.10 M NaCl solution in the cathode chamber was used in all experiments. The recirculation flow of the cathode solution was kept at 22 L h⁻¹ using a peristaltic pump (Watson Marlow,

UK). The anode liquid medium, domestic wastewater, was collected weekly from a local pumping station and stored at 4°C. Prior to use, 5 L of the domestic wastewater was heated up to ambient temperatures (24.3±0.5°C) and fed to the influent buffer tank. pH in the influent was measured using a pH probe (Ionode Pty Ltd., AU) and maintained at 7.5 during the experiment through a PLC controlled dosage of a 0.5 M NaOH solution. The wastewater was continuously recirculated. This fed batch system was used to minimize the amount of domestic wastewater needed (continuous feeding would have required significant amounts of wastewater per day). A concentrated sodium sulfide (Na₂S·9H₂O) stock solution (~5.5 g L⁻¹ sulfide-S), prepared according to [15], was continuously supplied to the incoming line of the anode chamber via a syringe pump (NE-1600, New Era Pump Systems, Inc., USA) at a dosing rate of ~36 mg sulfide-S h⁻¹, which was sufficient to give an anode influent concentration of ~10.0 mg S L⁻¹ by assuming that the recirculated wastewater contained no sulfide.

2.2 Measurements and calculations

Galvanostatic measurements and control were performed using a Wenking potentiostat/galvanostat (KP07, Bank Elektronik, gmbH, Germany). The anode, cathode potentials and the current were recorded every 60s using an Agilent 34970A data acquisition unit. The amount of sulfide dosed to the reactor can be expressed as a charge quantity expressed in Coulomb:

$$Q = nFc_{added} / M \quad (\text{Eq. 1})$$

With F the Faraday constant (96485 C mol⁻¹, n the number of electrons involved (i.e. 8 electrons for the oxidation of 1 mol sulfide to sulfate), c the amount of sulfide added (g) and M the molar weight of sulfide (i.e. 32 g mol⁻¹). Hence, by determining the coulombic efficiency (CE) based on the conversion of sulfide to sulfate the coulombic efficiency can be calculated as follows:

$$CE = \frac{nFc_{removed} / M}{nFc_{added} / M} = \frac{c_{removed}}{c_{added}} \quad (\text{Eq. 2})$$

2.3 Chemical analyses

Sulfide, sulfite, thiosulfate and sulfate concentrations were measured by Ion Chromatography (IC), using a Dionex 2010i system, according to [16]. Samples were immediately filtered using a 0.22 μ m syringe filter (Millipore, USA) and preserved in previously prepared Sulfide Antioxidant Buffer (SAOB) solution prior to ion chromatography analysis. SAOB solution was prepared using Helium purged MilliQ (18 M Ω) water, 3.2 g L⁻¹ NaOH and 2.8 g L⁻¹ α -ascorbic acid. After preparation, the solution was kept refrigerated, shielded from light and not used beyond 24 hours. Elemental sulfur was assumed to be the difference between the total sulfide added and the soluble sulfur species (i.e. sulfide, sulfite, thiosulfate and sulfate).

COD (range 25-1500 mg L⁻¹) and free chlorine (range 0-4 mg L⁻¹) concentrations were determined by means of cuvette tests (Merck, Germany). COD concentrations were corrected for the soluble sulfur species in the solution. The conductivity was measured using a hand-held meter (Cyberscan PC 300, Eutech Instruments). The produced gas (i.e. in-situ oxygen generation) was analysed using a Gas Chromatography (Shimadzu, Japan).

2.4 Experimental procedures

Experiments were divided into 2 different sets. The first set of experiments compared the performance of five different mixed metal-coated titanium electrode materials (Ta/Ir, Ru/Ir, Pt/Ir, PbO₂, SnO₂). Key focal points were (a) the kinetics of the sulfide oxidation, (b) possible oxidation of organics (i.e. COD), (c) the amount of excess in-situ generated oxygen and (d) the required energy input (i.e., based on the obtained cell potential) of the different electrode materials. The second set of experiments investigated the influence of chloride concentrations on (a) the kinetics of the sulfide oxidation, (b) possible oxidation of organics (i.e. COD) and (c) the required energy input (i.e. obtained cell potential) using Ru/Ir and Ta/Ir coated titanium as electrode material.

Each time, the performance was assessed during 6-hour experimental runs using galvanostatic control at a fixed current density of 10 mA cm⁻². This current density level was enough to oxidize all sulfide added to the system to sulfate. All experiments were performed in triplicate. Prior to each experiment, the head space of the influent buffer vessel was flushed with nitrogen for at least 5 minutes to obtain a head space that consisted of 100% nitrogen. In this way, any excess in-situ generated oxygen could be measured using Gas Chromatography after every experiment.

3. Results and discussion

3.1 Influence of electrode material on sulfide oxidation

The influence of the electrode material on the kinetics of anodic sulfide oxidation was investigated during 6-hour experiments at a fixed current density of 10 mA cm^{-2} . During the experimental runs, sulfide concentrations increased to approximately $7\text{-}10 \text{ mg L}^{-1}$ due to the recirculatory mode of operation. The typical profiles of the sulfide concentration are presented in the supplementary information S1. In Table 1 an overview of the results using Ta/Ir, Ru/Ir, Pt/Ir, PbO_2 and SnO_2 as electrode material are presented. The obtained removal and Coulombic efficiencies using Ta/Ir, Ru/Ir, Pt/Ir, PbO_2 and SnO_2 were 78 ± 5 , 77 ± 1 , 85 ± 4 , 83 ± 2 and $84\pm 1\%$, respectively. This is equal to sulfide removal rates of 10.8 ± 0.2 , 11.7 ± 1.1 , 12.4 ± 0.4 , 12.4 ± 0.4 and $12.9\pm 0.8 \text{ g S m}^{-2}_{\text{electrode surface}} \text{ h}^{-1}$. The obtained coulombic efficiencies were calculated based on the oxidation of sulfide to sulfate (see Equation 2).

The values observed for the sulfide removal rates expressed in $\text{mg S L}^{-1} \text{ wastewater h}^{-1}$ 7.5 ± 0.3 (Ta/Ir) to 7.8 ± 0.6 (SnO_2) are in agreement with the chemical sulfide oxidation rates found under high dissolved oxygen concentrations in domestic wastewater [17]. Furthermore, GC analysis of the produced gas at the end of every experiment showed that in all experiments similar amount of excess oxygen was generated and transferred to the headspace. The obtained excess oxygen generation using Ta/Ir, Ru/Ir, Pt/Ir, PbO_2 and SnO_2 was 65 ± 13 , 60 ± 17 , 69 ± 8 , 66 ± 17 and $47\pm 8 \text{ mg}$ (Table 1). In a previous study, we showed that direct sulfide oxidation at the electrode surface was negligible under the given operational conditions [6]. If reactive oxygen species were primarily responsible for sulfide oxidation, we would have expected sulfate being the primary product of oxidation, contrarily to the results (see Table 1). If oxygen would be the predominant reaction mechanism, a mixture of sulfur species would be expected. The results suggest that in-situ oxygen generation is significant and could be primarily responsible for the sulfide oxidation observed.

The materials used are known to have different overpotentials for oxygen evolution. This however does not necessarily mean that they will produce different amounts of oxygen. The formation of reactive oxygen species such as OH^\bullet radicals are intermediate products during the oxidation of water to oxygen. In the first step, adsorbed OH^\bullet radicals are formed on the electrode surface. In the second step, the adsorbed OH^\bullet interacts with the oxygen already present in the oxide anode to form physisorbed or chemisorbed ‘active oxygen’. In absence of

any oxidisable pollutant this ‘active oxygen’ subsequently produces oxygen [18]. Thus, the efficiency of the formation of reactive oxygen species does not only depend on the electrode material but also on the concentration of the pollutant and its reactivity towards oxidation. Especially at low pollutant concentrations, low Coulmbic efficiencies for the formation of reactive oxygen species have been observed [19], which means that high coulombic efficiencies for oxygen evolution can be expected. Considering the low sulfide (i.e. $\sim 10 \text{ mg L}^{-1}$) and organics concentrations (i.e. $380 \pm 140 \text{ mg L}^{-1}$) during the experiments, this could explain the similar sulfide removal and excess oxygen production rates for all electrode materials.

It should be noted that in this study a laboratory reactor was used rather than a real rising main system. Hence, our system differed from a real sewer system as such that in our system (a) a headspace was present and (b) in-situ generated oxygen was dissolved into only 5 L. Hence, we produced much more oxygen per unit wastewater. The above caused that oxygen was transferred to the headspace instead of remaining in the water phase.

The anode potentials remained constant during the course of all the experiments. The anode potentials for Ta/Ir, Ru/Ir and Pt/Ir (low overpotential for oxygen evolution) were 1.41 ± 0.08 , 1.42 ± 0.06 and $1.53 \pm 0.12 \text{ V vs. SHE}$, whereas the anode potentials for PbO_2 and SnO_2 were 1.80 ± 0.04 and $2.22 \pm 0.11 \text{ V vs. SHE}$, respectively. The overall cell voltage for all electrode materials, except for SnO_2 ($9.0 \pm 0.4 \text{ V}$), were approximately 5 V (Table 1). As yet, we have no explanation for the unexpectedly high cell voltage for SnO_2 , the use of this electrode apparently caused a higher ohmic resistance or higher cathodic overpotential.

The mechanism of the generation of oxygen active species is very complex and can involve the generation of several radical species containing oxygen and/or halogen atom (e.g. $\text{O}_2^{\bullet-}$, $\text{HO}_2^{\bullet-}$, HClO^{\bullet}) other than hydroxyl radicals which can occur at lower potentials. Hence, reactive oxygen species other than hydroxyl radicals might have been formed but did not have a significant impact on the sulfide removal process.

Table 1. Sulfide oxidation (n=3) from domestic wastewater using MMO coated titanium electrodes at a current density of 10 mA cm⁻².

parameter	unit	Ta/Ir	Ru/Ir	Pt/Ir	SnO ₂	PbO ₂
coulombic efficiency ^{a)}	%	78±5	77±1	85±4	84±1	83±2
removal efficiency	%	78±5	77±1	85±4	84±1	83±2
removal rate	g S m ⁻² _{electrode} surface hr ⁻¹	10.8±0.2	11.7±1.1	12.4±0.4	12.9±0.8	12.4±0.1
removal rate	mg S L ⁻¹ hr ⁻¹	7.5±0.3	7.7±0.5	7.7±0.2	7.8±0.6	7.8±0.7
total S added (mg)	mg	199±9	219±21	210±18	220±12	214±6
final sulfide conc.	mg L ⁻¹	7.9±2.6	10.0±1.2	6.2±2.3	6.6±0.6	6.9±1.8
S ⁰ produced	mg	100±9	97±4	108±19	136±25	101±36
S ₂ O ₃ ²⁻ produced	mg	63±9	64±13	52±6	43±10	50±8
SO ₃ ²⁻ produced	mg	0.9±0.2	1.5±0.5	1.1±0.7	0.8±0.5	1.1±0.7
SO ₄ ²⁻ produced	mg	10±5	14±15	34±16	28±8	30±17
COD removed	mg	199	256	204	274	117
COD removal rate	mg COD hr ⁻¹	43	33	34	46	26
O ₂ produced	mg	60±17	65±13	69±8	47±8	66±17
temperature	°C	24.5±0.5	24.1±0.4	24.6±0.4	25.0±0.6	24.3±0.4
conductivity	mS cm ⁻¹	1.11±0.01	1.15±0.01	1.17±0.06	1.16±0.04	1.09±0.09
chloride concentration	mg L ⁻¹	114±9	117±9	115±9	109±10	114±6
pH ^{b)}	-	7.5	7.5	7.5	7.5	7.5
average anode potential	V	1.41±0.08	1.42±0.06	1.53±0.12	2.2±0.11	1.8±0.04
average cell voltage	V	5.3±0.4	5.2±0.4	5.0±0.2	9.0±0.4	5.0±0.2

a) Coulombic efficiency is based on the oxidation of sulfide to sulfate

b) pH is controlled online

Figure 2 shows the electron distribution among the different electron sinks (i.e. sulfur, thiosulfate, sulfite, sulfate, excess oxygen and COD (i.e. organics) during the oxidation of sulfide using the different electrode materials. A significant part of the charge supplied to the system was used for the oxidation of organics. The charge used for the oxidation of organics was 46%, 60%, 47%, 64% and 36% for Ta/Ir, Ru/Ir, Pt/Ir, PbO₂ and SnO₂, respectively.

Concentrations of the different dissolved sulfur species (i.e. sulfide, sulfite, thiosulfate and sulfate) indicate that 43±2%, 39±7%, 47±8%, 42±11% and 57±10% of the total sulfide added was oxidized to elemental sulfur using Ta/Ir, Ru/Ir, Pt/Ir, PbO₂ and SnO₂, respectively. This is further supported by the reasonably small gap in the electron balances of the experiments (see Figure 2). No elemental sulfur was visually observed on the electrode surface. This

suggests that the elemental sulfur was formed in the bulk by means of indirect oxidation with oxygen.

In summary, the results highlight that under the applied operational conditions the sulfide removal process in terms of removal efficiency, excess oxygen generation, overall cell potential (except SnO_2) and electron distribution is not significantly influenced by the electrode material used.

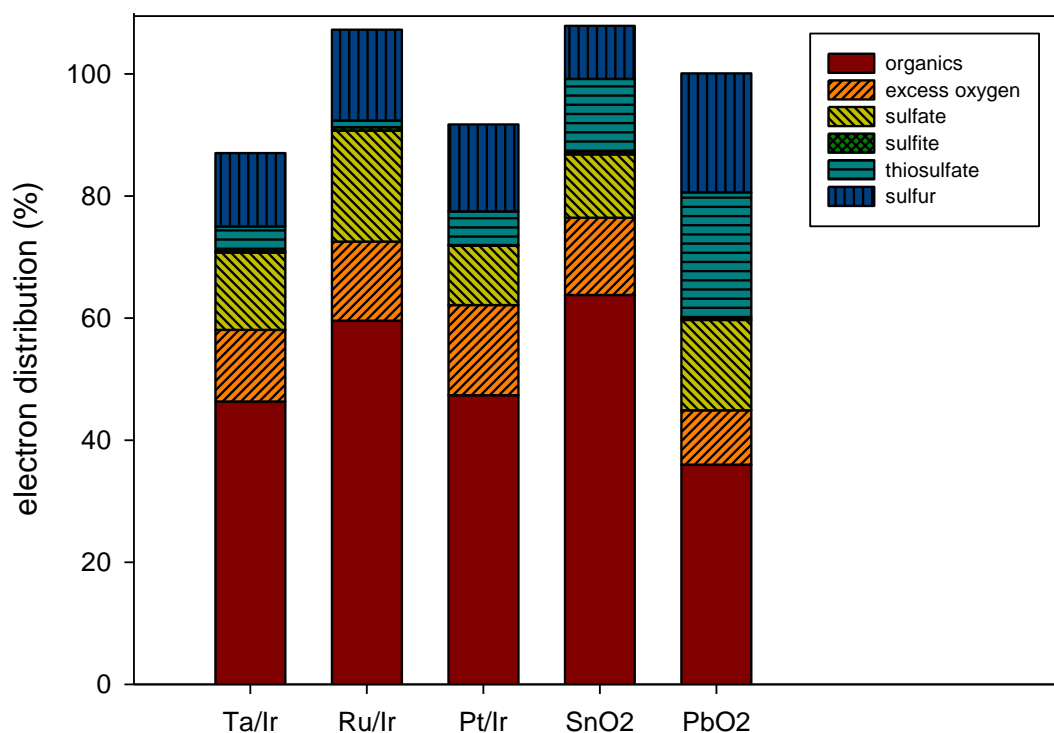


Figure 2. Electron distribution (%) among the different electron sinks (i.e. sulfur, thiosulfate, sulfite, sulfate, excess oxygen and organics) during the oxidation of sulfide using Ta/Ir, Ru/Ir, Pt/Ir, PbO₂ and SnO₂ electrodes at a current density of 10 mA cm⁻² (n=1).

3.2 Influence of chloride concentration on sulfide oxidation

The impact of elevated chloride concentration was investigated using Ta/Ir and Ru/Ir coated titanium electrodes; electrodes with a low and high reported catalytic activity towards chlorine generation, respectively. Table 2 shows that similar sulfide removal efficiencies and removal rates as in the experiments at low chloride concentrations were obtained (i.e. 7.7 ± 0.5 versus 7.0 ± 1.0 and 7.5 ± 0.3 versus 7.7 ± 0.3 mg S L⁻¹ h⁻¹). Figure 3 shows the electron distribution among the different electron sinks (i.e. sulfur, thiosulfate, sulfite, sulfate, excess oxygen and organics) during the oxidation of sulfide using of Ta/Ir and Ru/Ir electrodes, respectively. Similar to the experiments at low chloride concentrations a large part of the

charge supplied to the system was used for the oxidation of organics (i.e., 50±10, 50±8% for Ta/Ir and Ru/Ir, respectively).

Table 2. Sulfide oxidation (n=3) from domestic wastewater at elevated chloride concentrations using Ta/Ir and Ru/Ir coated titanium electrodes at a current density of 10 mA cm⁻².

parameter	unit	Ta/Ir	Ru/Ir
coulombic efficiency ^{a)}	%	87± 4	86±5
removal rate	g S m ⁻² electrode surface hr ⁻¹	12.9±1.0	12.2±1.2
removal rate	mg S L ⁻¹ hr ⁻¹	7.7±0.3	7.0±1.0
total S added (mg)	mg	213±8	203±8
final sulfide conc.	mg L ⁻¹	5.4±1.3	5.7±1.8
S ⁰ produced	mg	139±0	103±20
S ₂ O ₃ ²⁻ produced	mg	29±14	33±5
SO ₃ ²⁻ produced	mg	0.1±0.1	0.3±0.1
SO ₄ ²⁻ produced	mg	20±12	39±14
COD removed	mg	213±16	216±33
COD removal rate	mg COD hr ⁻¹	36±6	37±7
O ₂ produced	mg	77±19	65±10
temperature	° C	24.0±0.5	24±0.4
conductivity	mS cm ⁻¹	3.73±0.05	3.73±0.05
chloride concentration	mg L ⁻¹	1117±37	1119±25
pH	-	7.5	7.5
average anode potential	V	1.51±0.18 ^{a)}	1.43±0.03
average cell voltage	V	4.21±0.9 ^{a)}	4.64±0.2

a) n=2

Ru/Ir coated titanium electrodes are well-known for their low overpotential for chlorine generation. Hence, at high chloride concentrations in-situ chlorine generation may have an impact on the sulfide oxidation process and might also affect the removal of organics. The maximum chlorine generation under the mass transfer limiting conditions at a planar electrode (under optimum mixing conditions) can be described according to:

$$J_L = nFk_m[Cl^-] \quad (\text{Eq. 3})$$

Where J_L is the mass transfer limited current density (mA cm⁻²), n is the number of electrons involved (i.e. 1 for the oxidation of chloride to chlorine), F the Faraday constant (96485.3 C

mol^{-1}), k_m the mass transport rate coefficient (m s^{-1}) and Cl^- the chloride concentration (mg L^{-1}). Assuming a k_m of $0.8 \cdot 10^{-5} \text{ m s}^{-1}$ [20] and an average chloride concentration of 114 mg L^{-1} (i.e. the chloride concentration present in the sewage wastewater used) the mass transfer limited current is only 0.25 mA cm^{-2} . In addition, a migration current due to the migration in the chloride transport can be expected as result of the low conductivity of the wastewater [21]. However, at the applied current density (10 mA cm^{-2}), the chloride concentration and the applied electrical field the relative importance of the migration current density is small. The applied current density in all experiments is 10 mA cm^{-2} and thus sulfide oxidation by means of in-situ chlorine production is expected to be small. Hence, it is expected that at low chloride concentrations Ru/Ir coated titanium electrodes mainly will result in the in-situ generation of oxygen and hence similar kinetics for the anodic sulfide oxidation are expected.

However, at high chloride concentrations up to 1100 mg L^{-1} , which are often observed in sewers in many coastal areas, chlorine generation can play a significant role in the anodic sulfide removal process. Depending on the pH, sulfide can be oxidized by chlorine either to elemental sulfur or sulfate. At pH values ≤ 7.5 , sulfide is oxidized by chlorine to elemental sulfur [22]. Thus, under the conditions normally observed in sewer systems (i.e. $\text{pH} \leq 7.5$) the addition of chlorine would result in the oxidation of sulfide (HS^-) to elemental sulfur. The amount of sulfide dosed in the experiments was equivalent to 2.5 mA cm^{-2} when oxidized to sulfur), whereas the mass transport limited current for the generation of chlorine at chloride concentrations of 1100 mg L^{-1} is approximately 2.4 mA cm^{-2} .

Thus, under elevated chloride levels sufficient chlorine could have been produced to oxidize the sulfide added while this might not have been the case at low chloride concentrations. The results showed that at elevated chloride concentrations similar sulfide and organic removal rates were obtained (Table 2). Moreover, similar electron distribution among the electron sinks was observed. Hence, it appears that elevated chloride concentrations did not entail any significant differences in sulfide removal rate as well as in the organic removal. Analysis of the free chlorine concentration revealed that in all experiments no free chlorine or other reactive oxygen species (which are also detected with the used method) were present. It cannot be excluded that chlorine was formed and instantly reacted with the sulfide and/or organics present. This would be in line with several studies earlier reported [7, 21].

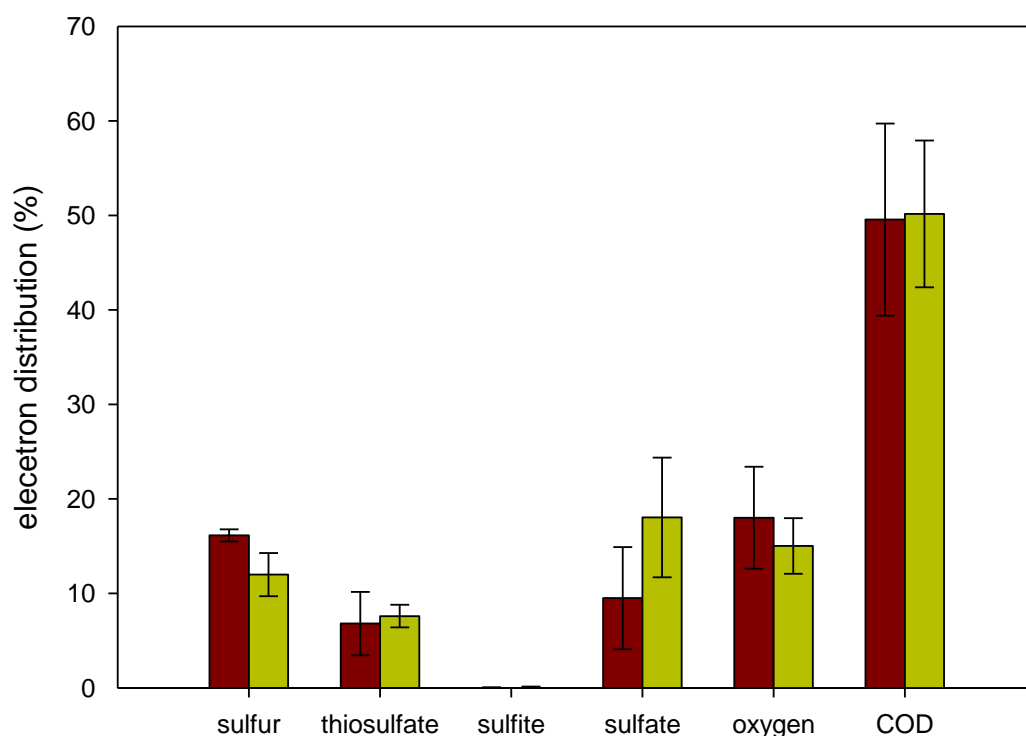


Figure 3. Electron distribution (in %) among the different electron sinks (i.e. sulfur, thiosulfate, sulfite, sulfate, excess oxygen and COD (i.e. organics)) during the oxidation of sulfide using Ta/Ir and Ru/Ir, electrodes at a current density of 10 mA cm^{-2} at high chloride concentrations ($n=3$).

3.3 Implications for practice

The results could indicate that sulfide removal by in-situ generated oxygen was the predominant reaction mechanism, independent of the electrode material used. Other reaction mechanisms including the formation of radical species containing oxygen and/or halogen atom (e.g. $\text{O}_2^{\bullet-}$, $\text{HO}_2^{\bullet-}$, HClO^{\bullet}) cannot be excluded but did not have a significant impact on the sulfide removal process. In perfectly mixed conditions, such as in a rotating disc setup, the different mechanisms for the electrodes would be observed to a higher extent. However, in the reactors here, which are more amenable to wastewater treatment, limitations exist on the mixing intensity.

Oxygen injection is presently considered as an attractive option for sulfide abatement in sewer systems. It is less expensive than most other chemicals, and can target rising mains where the SRB activity is the highest [5]. However, transport and storage of pure oxygen carries serious safety issues and precise control of dosing is not straightforward. By generating oxygen in-situ the requirement for transport and storage are avoided, thus mitigating safety concerns. Other advantages of in-situ oxygen generation compared to

traditional methods for oxygen supply are the fine dispersion, high controllability and the ease to monitor. The disadvantage is the cost of the oxygen per unit weight.

All electrode materials performed similarly in terms of sulfide removal. Therefore, Ta/Ir, Ru/Ir and Pt/Ir coated titanium electrodes seem the most suitable electrodes since they possess the lowest overpotential for oxygen evolution and they are already used in full scale applications. However, the life time of Ru/Ir electrodes for the oxygen evolution reaction, which is the predominant reaction at low chloride concentrations, is low [23]. Hence, Ta/Ir and Pt/Ir coated titanium electrodes appear the most suitable electrodes for sulfide oxidation from domestic wastewater in sewer systems.

Based on a cell potential of 5 V, a Coulombic efficiency of 95% (for oxygen generation) and a cost of \$0.06 per kWh, the estimated delivery cost is \$1.06 per kg, relative to a delivery cost of \$0.54-0.82 per kg for standard oxygen purchases [24]. However, standard oxygen injection in sewer systems has low efficiency (i.e. ~20 to 40%) [24] since oxygen is often dosed in an inefficient way (i.e., coarse bubbles) which results in a significant loss of undissolved gas from air in gas release valves downstream. The latter is avoided when oxygen is generated in-situ due to the high transfer efficiency and fine dispersion of in-situ generated oxygen. The deployment of a sulfide or dissolved oxygen sensor before or after the electrochemical system respectively would also allow further fine-tuning of the oxygen dosing. While entailing a higher cost, sustainable electricity solutions such as photovoltaic power would allow total independence of the dosing system of transport or utility requirements. An in-depth life cycle analysis would provide more insight into the sustainability of the existing dosing methods.

In all experiments excess oxygen was produced, which in a practical situation would be used for chemical oxidation or by the biofilm in the sewer pipes for biological sulfide oxidation or the removal of organic matter. Nonetheless, in this study, the impact of electrode material and chloride concentration on the kinetics of sulfide oxidation from real domestic wastewater was successfully investigated.

Over the course of the experiments, none of the electrode materials deteriorated or demonstrated changing potential over time. Earlier studies at lower current densities indicated electrode fouling with sulfur [25-27], it appears that at the higher current densities used here sulfur either flakes off or is further oxidized to its soluble forms. However, in realistic conditions of the sewer, other forms of fouling such as ragging, particle settling and scaling

may occur. Long term trials on site are presently underway to investigate these possible impacts, which were not observed here.

Scaling of the membrane and the electrode surface, on the other hand, was observed in the cathode chamber. This is caused by transport of bivalent cations such as calcium through the cation exchange membrane causing precipitation of inorganics such as calcium hydroxide or calcium carbonate [28]. To overcome problems with scaling the cathode needs to be cleaned periodically. This can be done either by chemical cleaning (i.e. the addition of citric or hydrochloric acid) or by periodic switching of the polarity of the electrodes (anode becomes cathode/cathode becomes anode), the latter option is attractive from an operational perspective but does restrict the types of electrodes that can be used.

4. Conclusions

In this study, we investigated the kinetics of sulfide oxidation from real domestic wastewater using five different types of mixed metal-coated titanium electrodes (Ta/Ir, Ru/Ir, Pt/Ir, SnO₂ and PbO₂) at a current density of 10 mA cm⁻². The obtained sulfide removal efficiencies were not significantly influenced by the electrode material used. The results indicate that, independent of electrode material used, sulfide was removed by means of chemical oxidation with in-situ generated oxygen. Ta/Ir and Pt/Ir appear the most suitable electrodes since they have a low overpotential for oxygen evolution and are known for their stability even at low chloride concentrations. The obtained sulfide removal rates were in the same order of chemical rates found under high oxygen concentrations whereas in all experiments excess oxygen was produced. Elevated chloride concentrations did not entail any significant difference in sulfide removal rate. Analysis revealed that no free chlorine was present even at high chloride concentrations.

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Systems”). The authors also want to acknowledge Dr. Beatrice Keller-Lehmann and Ms. Susan Cooke for their helpful collaboration with the chemical analyses.

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Supplementary Information:

**Electrochemical sulfide oxidation from domestic
wastewater using mixed metal coated titanium
electrodes**

S1: Typical sulfide generation profiles during sulfide oxidation from domestic wastewater using Ta/Ir, Ru/Ir, Pt/Ir, PbO₂ and SnO₂ electrodes. A concentrated sulfide solution was continuously added to the domestic wastewater. The domestic wastewater was continuously recirculated over the influent buffer vessel (5 L). Consequently, an increase in sulfide concentration will be observed during the course of the experiments if sulfide removal efficiencies are lower than 100%. In Figure 1A to 1E the sulfide profiles obtained during the oxidation of sulfide using Ta/Ir, Ru/Ir, Pt/Ir, PbO₂ and SnO₂ coated titanium electrodes are presented.

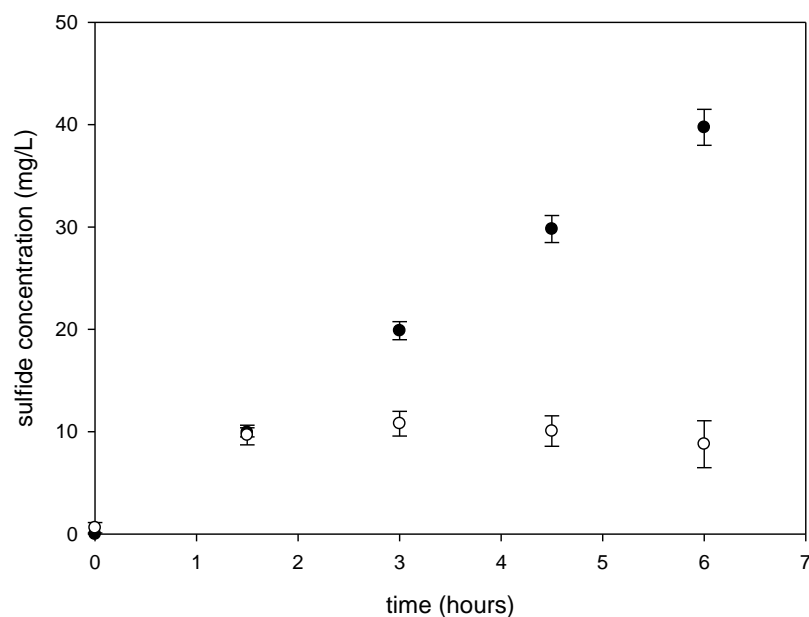


Figure 1A: Ta/Ir

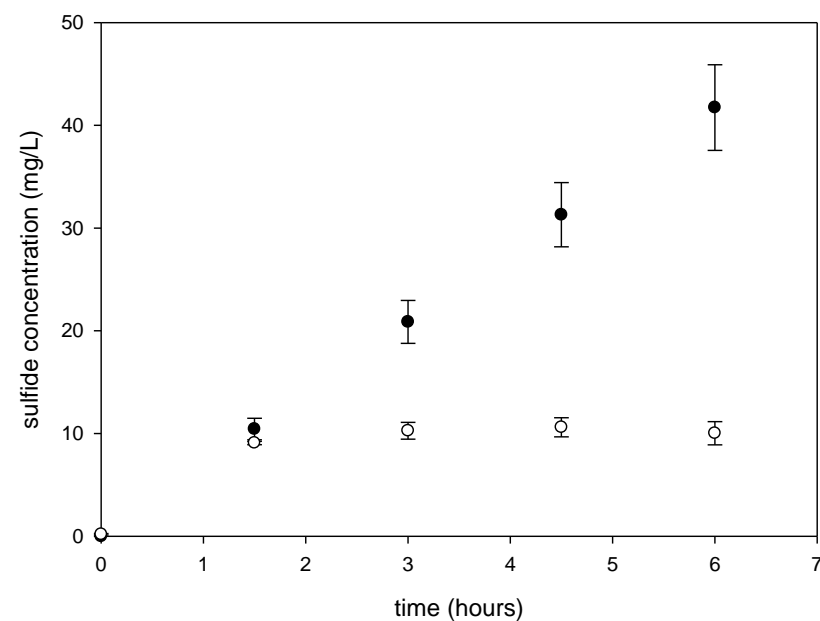


Figure 1B: Ru/Ir

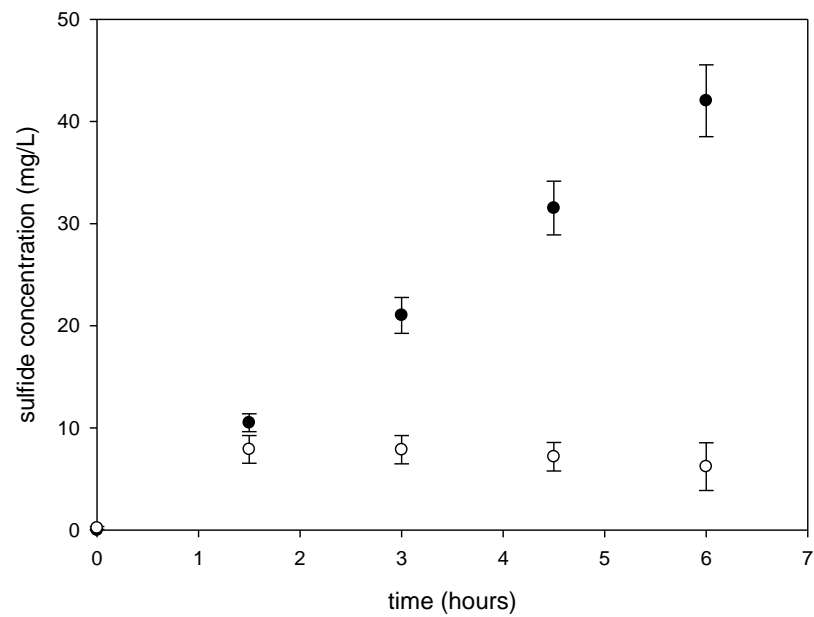


Figure 1C: Pt/Ir

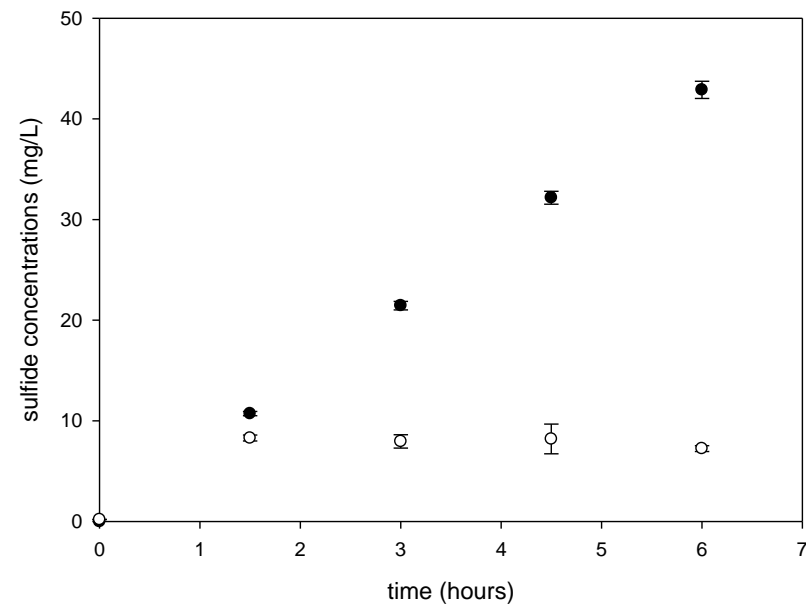


Figure 1D: PbO₂

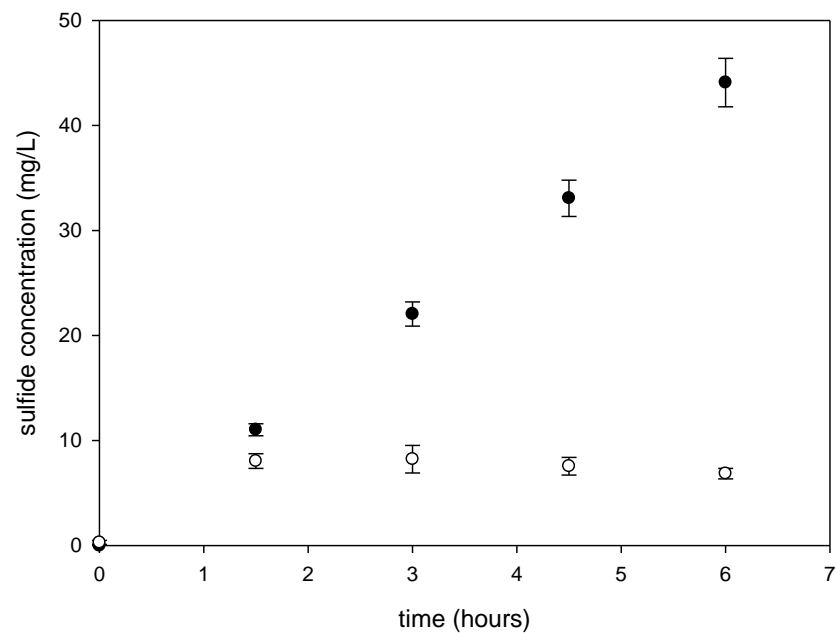


Figure 1E: SnO₂

Figure 1A-E. Typical sulfide generation profile during sulfide oxidation from domestic wastewater at a current density of 10 mA cm⁻² (n=3)
(●) sulfide dosed and ○ measured sulfide concentration (mg L⁻¹).

APPENDIX C

Electrochemical caustic generation from sewage

Authors: Ilje Pikaar, René A. Rozendal, Zhiguo Yuan and Korneel Rabaey

Electrochemistry Communications, Accepted

Abstract

Sewer corrosion caused by hydrogen sulfide generation represents a major issue in sewer management. One commonly used approach for mitigation is the periodic dosing of caustic to the sewer. This creates elevated pH levels that inactivate/kill sulfate reducing bacteria (SRB) present in the biofilms on the sewer pipe. In this study, we investigated the in-situ electrochemical generation of caustic from sewage. The average coulombic efficiency for caustic generation was $53\pm 8\%$ ($n=10$) at a current density of 10 mA cm^{-2} . The average required cell voltage input was 5.2 ± 0.7 Volt. Over time, this voltage increased due to a membrane fouling associated increase of the ohmic resistance of the cell. Switching the polarity of the electrodes every four hours was effective to control this fouling and thus retain a stable voltage requirement. This process constitutes a promising reagent-free method for sulfide abatement in sewers.

keywords: sewage, caustic, sewer corrosion, polarity switching

1. Introduction

Sewer corrosion caused by hydrogen sulfide generation represents a major issue in sewer management. A recent industry survey revealed that the addition of caustic to reach toxic levels (i.e. $\text{pH}>10.5$ to kill/inactivate the sulfate reducing bacteria is commonly used by the Australian water industry for sulfide control in sewers [1]. However, despite its strong benefits, this method also has some important disadvantages, including the frequent transport,

handling and storage of concentrated caustic, all of which constitute serious occupational health and safety hazards.

Caustic is normally produced via the chlor-alkali process, in which chlorine is produced from a concentrated brine solution at the anode while caustic is generated at the cathode. If not brine, but wastewater is used at an anode medium, it should theoretically also be possible to generate caustic directly from wastewater. It has indeed been shown that wastewater can be used as an anode medium [2]. Other studies have shown that urea from urine [3] and sulfide [4, 5] could be used as anodic electron donors. While current flows, cations such as Na^+ and K^+ instead of protons could migrate from anode to cathode through a cation exchange membrane. This would produce a caustic solution in the cathode.

In this study, we aim to experimentally demonstrate the direct electrochemical production of caustic from sewage in the context of sewer corrosion abatement. We also report and demonstrate a strategy based on periodic polarity switching of the electrodes to overcome the scaling problem caused by the migration of multivalent cations through membrane.

2. Experimental

2.1 Electrochemical cell and operation

The two-chambered electrochemical cell consisted of two Perspex frames separated by a cation exchange membrane (Ultrex CM17000, Membranes International Inc., USA). The internal dimensions of the anode and cathode compartment were $20 \times 5.0 \times 0.9$ cm creating an anode and cathode volume of 90 mL. Mesh shaped Pt/Ir coated titanium electrodes with a projected surface area of 24 cm^2 were used as the anode and cathode material (Magnet Special Anodes BV, The Netherlands). The anode and cathode were either located directly at the membrane surface or spacers (surface area: 24 cm^2 , thickness: 1 mm and mesh size: 3 mm) were placed between the membrane and electrode surface. In all experiments, an Ag/AgCl reference electrode (+197 mV versus NHE) was used. Sewage was fed to the anode chamber at a flow rate of 9.1 L h^{-1} , resulting an anode hydraulic retention time (HRT) of 0.6 min. At this flow rate, the applied current density corresponded to an anode-to-cathode-flux of 15-25% of the sodium present in the sewage. A recirculation flow of 60 L h^{-1} was applied to obtain a good mixing rate in the anode chamber. Domestic sewage was used as feedstock for the anode. 120 mL of a 10 g L^{-1} NaCl solution was fed to the cathode chamber and

replaced after every batch (4 hours). A water-lock (100 mL) containing 0.05 M HCl was used to trap any ammonia (NH_3) that may strip from the cathode solution as ammonium ($\text{NH}_4\text{-N}$).

The experiments were controlled galvanostatically using a Wenking potentiostat/galvanostat (KP07, Bank Elektronik, Germany). Two series of experimental runs were performed. The first series ($n=10$) was performed to determine the coulombic efficiency of caustic generation at a current density of 10 mA cm^{-2} , the required energy input (i.e. the obtained cell voltage) per unit caustic produced, and the feasibility of polarity switching to avoid scaling. After each experimental run of 4 hours the polarity of the cell was switched, i.e. the anode of the previous experimental run became the cathode of the subsequent experimental run and vice versa. In the second series of experiments ($n=3$), spacers were used to investigate their impact on (a) the coulombic efficiency for caustic generation and (b) the cell voltage. Also here, polarity switching every 4 hours was used.

The anode and the cathode potentials were recorded every minute using an Agilent 34970A data acquisition unit. The coulombic efficiency (CE) was calculated as the ratio between the amount of charge transfer used for the production of caustic (based on the one electron reduction of water to hydroxide) and the total charge added to the system. All electrode potentials are reported versus NHE.

2.2 Chemical analyses

The pH of the cathode compartment was determined by alkalinity titration using a 1 M hydrochloric acid solution at the end of every batch. The conductivity and temperature were measured by using a handheld conductivity meter (Cyberscan PC 300, Eutech Instruments). Ammonium concentrations were analysed using a Lachat QuikChem8000 (Lachat Instruments, USA) flow injection analyser (FIA). Elements (e.g. Sodium and Calcium) were measured with inductively coupled plasma optical emission spectrometry (Perkin Elmer ICP-OES Optima 7300DV, Perkin Elmer, USA). Chloride concentrations were measured with Ion Chromatography (IC) using a Dionex 2010i system.

3. Results and discussion

3.1 Caustic generation from sewage

During 4-hour experiments, we investigated the direct production of caustic from sewage at a current density of 10 mA cm^{-2} . The results showed that the obtained caustic concentration

was 0.61 ± 0.10 (n=10) wt % at a CE of $53 \pm 8\%$ (without the use of spacers). Due to the very short HRT applied in the anode (0.6 min), no significant pH change in the sewage was observed. Our previous studies performed under similar conditions showed that the production of oxygen from water was the primary anodic reaction and the formation of chlorine from chloride was negligible [4, 5]. As the cathode is fed with clean water, the only cathodic reaction that takes place is the reduction of water to hydrogen and hydroxide. A CE lower than 100% implies that either (i) protons and/or ammonium migrated from anode to cathode, or (ii) hydroxyl ions diffused back from cathode to anode. Analysis of the ammonium concentrations at the cathode revealed that there was insignificant transport of ammonium (Table 1). Hence, the transport of protons and/or back-diffusion of hydroxyl likely caused the decrease in CE.

Table 1. (Waste)water characteristics of the anode and cathode compartment

parameter	unit	anode	cathode ^{a)}
sodium	mg L ⁻¹	119±28	1526±554
potassium	mg L ⁻¹	21±6	337±70
magnesium	mg L ⁻¹	14±7	33±23
calcium	mg L ⁻¹	33±3	418±101
ammonium (as N)	mg L ⁻¹	35±7	2.3±2.2
chloride (t=0)	mM	n.d.	171
chloride (t=end)	mM	n.d.	138±4.5
pH	-	7.2±0.1	13.3±0.04
OH (t=end)	mM	n.d.	199±18
NaOH conc. wt %	%	-	0.61±0.1
conductivity	mS cm ⁻¹	1.05±0.12	25.3±3.1
temperature	C	25.1±1.0	n.d.

^{a)} Concentrations after 4 hours.

Protons are generated in the anodic reaction. At high current densities, this can result in high proton concentrations in close vicinity of the anode surface. As the anode is located directly at the membrane surface, these high proton concentrations could cause a significant migrational proton transport from anode to cathode, even though the average anodic concentration of protons compared to other cations is low. Thus, increasing the distance between anode and membrane, and thereby locally improving mixing conditions, may lead to reduced migrational proton transport and hence a higher caustic recovery. The obtained

caustic recovery using spacers was $46\pm 7\%$ ($n=3$). Hence, either the use of spacers did not improve the mixing conditions or back-diffusion of hydroxyl ions from the cathode to the anode also played an important role.

Chemical analysis of the elements and ammonium revealed that the transport of cations was not sufficient to maintain electroneutrality of the solution. Chloride analysis ($n=3$) revealed that there was significant back-diffusion of chloride towards the anode compartment (Table 1). As the hydroxyl concentration is in the same range as the chloride concentration (Table 1) it can therefore be expected that the hydroxyl back-diffusion is of the same order of magnitude as the chloride back-diffusion and thus significantly affects the caustic recovery. The distribution of the average transport of the cation and back-diffusion of anion species is presented in Table 2.

Table 2. Distribution of cation and anion transport at a current density of 10 mA cm^{-2} using sewage as anolyte solution and a 10 g L^{-1} NaCl solution as the catholyte ($n=3$).

component	percentage
sodium	$23.2\pm 2.5\%$
calcium	$5.8\pm 2.0\%$
potassium	$2.4\pm 0.3\%$
magnesium	$1.0\pm 0.6\%$
chloride back diffusion	$22.9\pm 2.1\%$
proton cross-over or hydroxide back diffusion	$44.7\pm 1.9\%$

a) The fraction of proton cross-over and/or hydroxide back diffusion is assumed to be equal to the total coulombs added $-\Sigma$ cation transport to cathode – chloride back diffusion.

Figure 1A and 1B show the anode, cathode and overall cell potentials during the experiments without and with spacers. In all experimental runs the anode and cathode potentials remained constant over the course of the experiments and were 1.8 ± 0.1 and -0.8 ± 0.02 Volt, respectively. However, the overall cell potential increased over the course of all experimental runs. In the experimental runs without spacers (Figure 1A), the average cell potential at the start of a cycle was 4.5 ± 0.2 Volt and increased to 5.9 ± 0.5 Volt by the end of the cycle, whereas in the experimental runs with spacers (Figure 1B), the average cell potential at the start of a cycle was 5.4 ± 0.4 Volt and increased to 8.3 ± 0.6 Volt by the end of the cycle. Hence, the use of spacer resulted in an increase in the average cell voltage from 5.2 ± 0.7 (no spacers) to 6.8 ± 0.2 Volt (with spacers). This increase can be explained from the

low conductivity of domestic wastewater ($\sim 1 \text{ mS cm}^{-1}$), which theoretically results in an increase in cell potential of $\sim 1 \text{ V}$ per mm distance between the anode and cathode at a current density of 10 mA cm^{-2} [6].

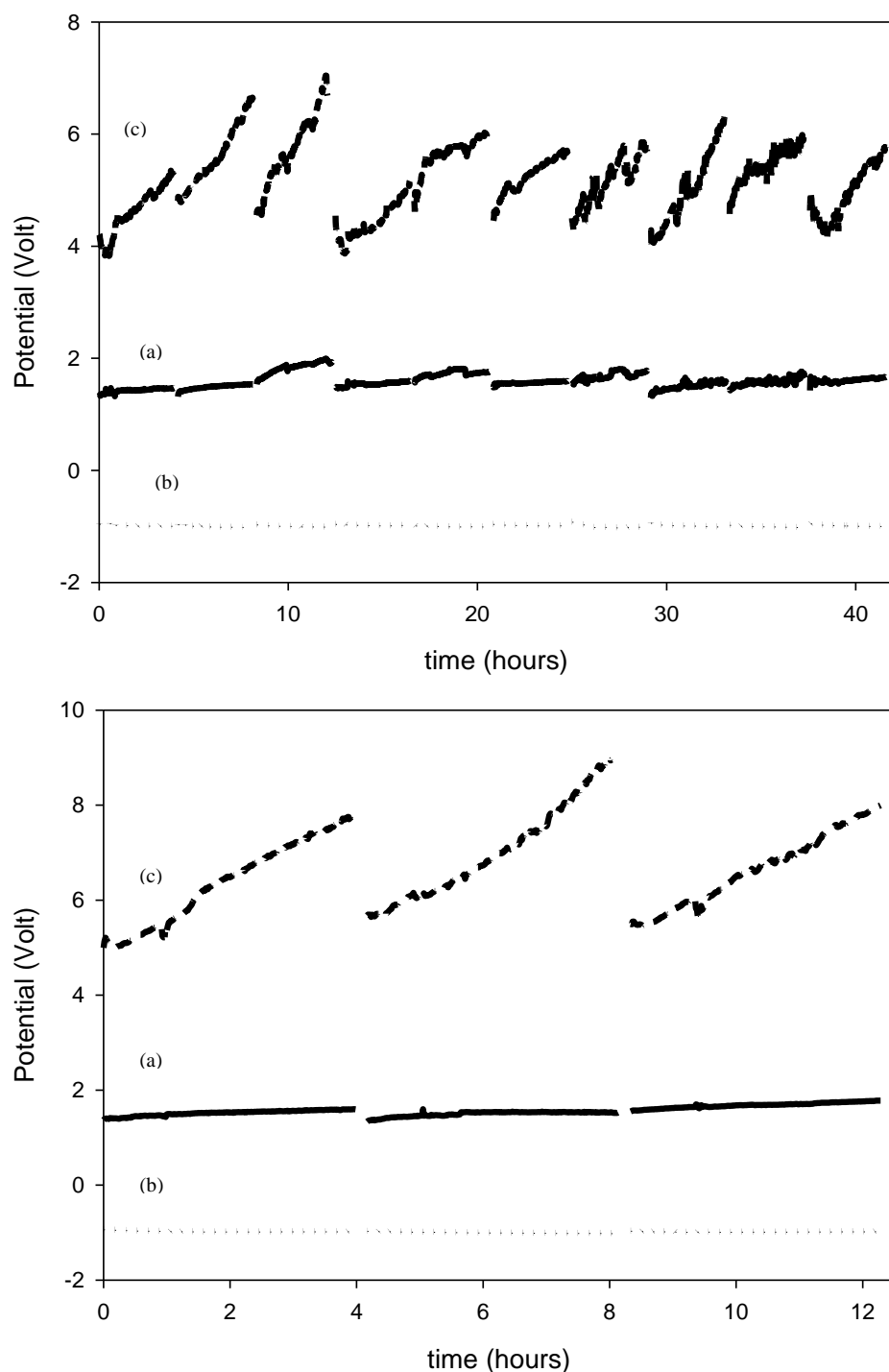


Figure 1. Typical profile of the (a) anode potential, (b) cathode potential and (c) cell voltage: (A) without spacers (n=10) and (B) with spacers (n=3).

Since the anode and cathode potentials remained constant, the increase in overall cell potentials over time were caused by an increase in membrane resistance due to the transport of bivalent cations like calcium to the cathode causing blockage of the membrane by precipitation of inorganics. This hypothesis was supported by the ICP analysis, which showed transport of calcium and magnesium to the cathode compartment (Table 2). In addition, scaling was visually observed on the membrane surface by the end of each cycle. The experiments showed that switching the polarity of the electrodes every 4 hours returned the cell potentials to their original values (see Figure 1A). Moreover, the observed scaling disappeared. Hence, it seems that periodic polarity switching is successful to prevent scaling, and thus avoids the necessity for frequent chemical cleaning. Further research is warranted to elucidate the impact of the switching and scaling on the electrode and membrane lifetime.

The results showed that it is feasible to produce caustic from sewage without significant pH changes at the anode. To the author's best knowledge, this is the first time that caustic is directly generated from sewage, potentially leading to a reagent free method for sulfide abatement in sewer systems.

3.2 Implications for practice

In this study, we experimentally demonstrated the feasibility of caustic generation from sewage. In a practical situation, the anode solution (sewage) is operated continuously with a short HRT (minutes), whereas the cathode is discharged/replenished discontinuously, letting the caustic accumulate over a period of days between discharges. As such, a strong caustic solution can be produced in the cathode without inducing significant changes in pH in sewage. When a sufficient amount of caustic is produced it can be dosed to the sewer to create a peak pH for a short period (e.g. 2 hours) to deactivate sewer biofilm. According to our calculations, the cost would be \$0.83-1.17 (kg S⁻¹) compared to \$1.7-7.2 (kg S⁻¹) [7] for conventional sulfide abatement strategies. The costs are based on the obtained results (i.e. CE and cell voltage) and a required caustic dosing frequency of once per week to pH 11. Our cost calculation indicated that taking into account the low conductivity of sewage a current density of 10 mA cm⁻² is a good starting point. Further research is underway to further optimize the operational parameters.

The results indicate that there was significant cross-over of protons as well as back-diffusion of anions. Further optimization of the process can occur by selecting ion exchange

membranes less prone to back-diffusion, such as the ion exchange membranes that are used in the chlor-alkali industry [8].

To reduce the explosive potential of H₂ formed in the cathode, we propose to sparge air through the cathode compartment.

Continuous experiments to determine the long-term performance at larger scale are required to accurately assess the potential of this method. The CE, cell voltage, attainable caustic concentration and the electrode life time will be critical parameters.

4. Conclusions

Caustic can be produced from sewage using Pt/Ir coated titanium electrodes at a current density of 10 mA cm⁻², with a coulombic efficiency of 53±8% at an average cell voltage of 5.2±0.7 Volt. Periodically switching the polarity of the electrodes was a successful method to overcome problems with scaling. The use of spacers did not increase the caustic recovery, but rather increased the cell voltage and thus energy input. This technology constitutes a promising reagent free method for sulfide abatement in sewer systems.

Acknowledgements

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APPENDIX D

Long-term field test of an electrochemical method for sulfide removal from sewage

Authors: Ilje Pikaar, Eugena Li, René A. Rozendal, Zhiguo Yuan, Jürg Keller and Korneel Rabaey

Water Research, waiting for project approval for submission

Abstract

Corrosion caused by hydrogen sulfide leads to significant costs for the rehabilitation or replacement of corroded sewer pipes. Conventional methods to prevent sewer corrosion normally involve the dosing of significant amounts of chemicals with the associated transport and storage costs as well as considerable maintenance and control requirement. Recently, a novel chemical free method for sulfide abatement based on electrochemical sulfide oxidation was shown to be highly effective for the removal of sulfide from synthetic and real sewage. Here, we report on the electrochemical removal of sulfide using Ta/Ir and Pt/Ir coated titanium electrodes under real sewer conditions during field trials. The results showed that sulfide can successfully be removed to levels below the normal target value at the end of a simulated rising main (i.e. $<1 \text{ mg L}^{-1}$). A coulombic efficiency for dissolved oxygen generation of $\sim 60\%$ was obtained and was independent of the current density. Scaling of the electrode and the membrane was observed in the cathode compartment and as a result the cell potentials increased over time. The cathode potentials returned to their original potential after switching the polarity every 2 days, but a more frequent switching would be needed to reduce the energy requirements of the system. Accelerated lifetime experiments indicated that a lifetime of 6.0 ± 1.9 years can be expected under polarity switching conditions at a pH of 14 and significantly longer at lower pH values. As operating the system without switching

simplifies construction as well as operation, the choice whether to switch or not will in practice depend on operational cost (higher/lower energy) versus capital cost (reactor and peripherals). Irrespective of the approach, our study demonstrates that electrochemical sulfide control in sewer systems may be an attractive new option.

keywords: Electrochemical oxidation, sulfide, sewer corrosion, sewage, anode

1. Introduction

Hydrogen sulfide generation is the main cause of sewer corrosion resulting in significant costs for the rehabilitation and/or repair of corroded sewer pipes [1]. Commonly used strategies to prevent sewer corrosion involve the prevention of anaerobic conditions by the addition of oxidants such as oxygen, nitrate and nitrite [2-5], the precipitation of sulfide with iron salts (FeCl_3 or FeSO_4^{2-}) [6-9] and the chemical oxidation of sulfide by the addition of oxygen, hydrogen peroxide, chlorine and ozone [1, 10, 11]. These methods are often cost prohibitive due to the requirement for continuous dosing of large amounts of chemicals.

Of the currently used methods oxygen injection is seen as one of the most attractive since it is relatively cost effective for targeting rising mains where the sulfide generation is the highest [5]. However, conventional oxygen injection often exhibits low oxidation efficiency [2], as a significant amount of undissolved oxygen is typically lost from the sewer system [12]. Furthermore, conventional oxygen injection comes with the necessity for frequent transport and storage of liquid oxygen, which poses a serious safety issue.

Previously, we showed that sulfide can be efficiently removed from synthetic and real sewage using Ta/Ir coated titanium electrodes [13]. In a second study, we investigated the effectiveness of 5 different mixed metal coated titanium electrodes with different electrocatalyst for sulfide removal [14]. The results indicated that sulfide oxidation by means of in-situ generated oxygen was the predominant reaction mechanism independent of electrode material used. By generating oxygen in-situ the transport and storage of oxygen are avoided. Moreover in-situ generated oxygen is expected to have a much higher transfer efficiency due to the fine dispersion (i.e. 1-30 μm) [15].

In these previous laboratory studies, a reactor was used in which synthetic or real sewage (5 L) was continuously recirculated over the electrochemical cell during 6-hour experiments, while sulfide was continuously added to simulate sulfide production. This approach was taken to avoid the use of unpractical volumes of wastewater in a laboratory. Due to the

continuous recirculation of the anolyte, the sulfide concentrations increased over time, whereas more oxygen per unit wastewater was produced. In addition, oxygen was also transferred to the headspace instead of remaining in the water phase, which decreased its effectiveness.

It was also shown that membrane fouling, which caused increased cell potentials as result of an increase in ohmic resistance, could be successfully prevented by switching the polarity every four hours [16]. However, frequent polarity reversal could negatively impact on the electrode lifetime [17]. Also, elevated pH values obtained in the cathode could negatively impact on the electrode lifetime. Furthermore, (bio)fouling, ragging and particle settling, which were not observed during laboratory scale experiments, may occur under realistic sewer conditions.

The aim of this study was to establish the effectiveness of electrochemical sulfide removal in sewers by demonstrating its working principle and the long-term performance under real sewer conditions. To the author's best knowledge, this is the first time that the long-term performance of electrochemical sulfide oxidation from sewage under real sewer conditions was investigated. In addition, we investigated the feasibility of periodic polarity switching every two days to overcome scaling issues. We also assessed the impact of the pH and polarity reversal on the electrode lifetime during accelerated lifetime experiments.

2. Experimental

2.1 Electrochemical cell and operation

Two electrochemical cells were constructed according to [13] (Figure 1). In the anode chamber, a mesh shaped Ta/Ir ($\text{TaO}_2/\text{IrO}_2$: 0.35/0.65) or a Pt/Ir ($\text{PtO}_2/\text{IrO}_2$: 0.70/0.30) anode was used (Magneto Anodes B.V., The Netherlands), depending on the experimental run performed. Both electrode materials had a thickness of 1 mm and a specific surface area of $1.0 \text{ cm}^2 \text{ cm}^{-2}$. A fine mesh stainless steel electrode with a stainless steel current collector (6 mm mesh size, 0.8 mm wire connected via a 6 mm stainless steel rod) or a mesh shaped Pt/Ir electrode was used in the cathode chamber, depending on the experimental run performed. The projected surface area of both the anode and cathode was 24 cm^2 (48 mm by 50 mm).

The influent flow rate of the domestic wastewater to both anode chambers was kept at 3.6 L h^{-1} using a peristaltic pump (Watson Marlow, UK). At this flow rate and current density applied to the system, the oxygen concentration would be 20 mg L^{-1} in case all electrons are

directed towards in-situ oxygen generation. A recirculation flow of 60 L h^{-1} was applied to obtain sufficient mixing (Figure 1). PVC tubing with an internal diameter of 8 mm was used for both anode and cathode feeding and recirculation lines. The domestic wastewater was sourced from a rising main of the Elanora sewer system (Gold Coast, Australia). Wastewater was first fed into a storage tank (110 L). An overview of the wastewater characteristics is presented in Table 1. The inlet point of the rising main was flushed for 10 seconds every 15 minutes with compressed air to minimize blockage of the inlet point. The cathode liquid consisted of a 2.5 g L^{-1} NaCl solution, which was continuously added to the cathode compartment at a flow rate of 3.6 L h^{-1} to minimize the pH increase in the cathode chamber (i.e. possibly reduce scaling) as a frequent polarity reversal could not be tested in the field as described in section 3.3. An Ag/AgCl (RE-5B, Bio Analytical, USA) reference electrode (assumed +0.197 V vs. SHE) was placed in the anode and cathode compartment in order to measure the anode and cathode half cell potentials. The cathode potentials were either measured relative to the reference electrode in the anode (i.e. cathode potential including ohmic losses) or relative to the reference in the cathode compartment (i.e. actual cathode potential). The anode and cathode potentials were monitored every 5 minutes using a data acquisition unit (34970A Data Acquisition Unit, Agilent Technologies, USA). The electrochemical cells were galvanostatically controlled using two Wenking potentiostat/galvanostat (KP07, Bank Elektronik, Germany) at a current density of $7.5\text{-}10 \text{ mA cm}^{-2}$. The coulombic efficiency was based on the conversion of sulfide to sulfate and determined according to Pikaar *et al.* (2011) [13].

A PVC tube with an internal diameter of 25 mm and a length of 10 meters was connected to the outlet of each anode to collect the effluent. This pipe was used to mimic a ‘rising main’ (i.e. plug flow in absence of a headspace) with a hydraulic retention time (HRT) of 1 hour and 20 minutes. Sulfide production in a rising main has previously been found to be approximately proportional to the A/V (biofilm surface to wastewater volume ratio) and the HRT [18]. The A/V ratio of the PVC tube is 160 m^{-1} ($= 4/0.025 \text{ m}$). Therefore, sulfide production in the PVC tube is expected to be equivalent to that in a rising main pipe with a diameter of 200 mm ($A/V = 20 \text{ m}^{-1}$) and an HRT of 10.6 hours. In the context of this paper, where O_2 generated in-situ is discharged to the rising main to oxidise sulfide and to prevent sulfide formation, the oxygen consumption rate of the tube would also be equivalent to that of a 200 mm pipe with a retention time of 10 hours. The system was flushed 1-3 times a week to remove solids that may have accumulated in the ‘rising mains’ due to the low up flow

velocity applied. The shear force incurred is not expected to remove biofilms developed on the inner surface of the pipe.

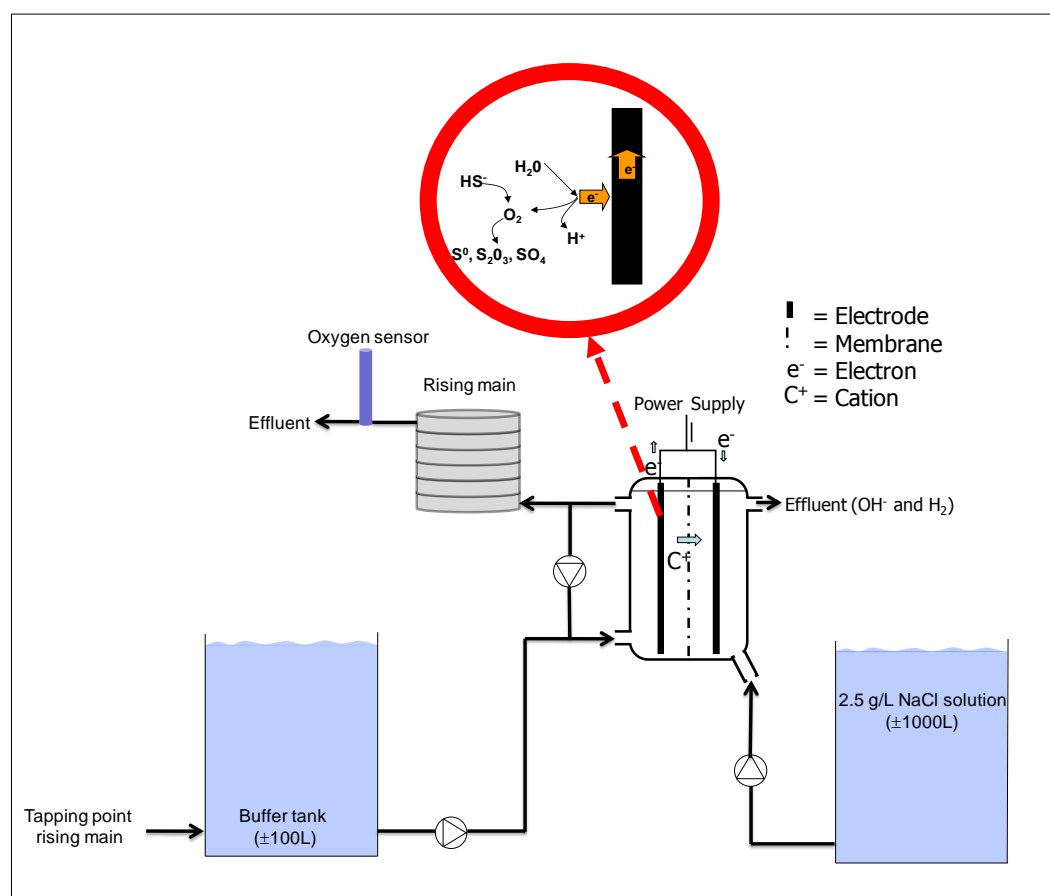


Figure 1. Schematic overview experimental setup field trials. Only one electrochemical cell is shown as two identical reactors were used in the experiments.

2.2 Experimental procedures

The field trials were performed using two identical reactors and divided into three different sets of experiments. In the first set of experiments, the coulombic efficiency for the in-situ generation of dissolved oxygen was determined using Ta/Ir coated titanium electrodes. The oxygen concentration was measured every 5 minutes during 45 minutes, directly at the outlet of the electrochemical cell. This was done prior to the start of the long-term experiment and also after 80 days of operation. The experiments were performed at three different current densities (i.e. 5.0, 7.5 and 10 mA cm^{-2}) to investigate the impact of the current density on the dissolved oxygen concentration. In the second set of experiments, (i) the feasibility of the electrochemical process in terms of sulfide removal efficiency, (ii) the required energy input and (iii) the impact of scaling were investigated using Ta/Ir coated electrodes at a current

density of 7.5-10 mA cm⁻². During this second experimental run, the cathode chambers were periodically rinsed with an 0.01M HCl solution to dissolve inorganics (e.g., calcium and magnesium) from both the electrode and membrane surface. Finally, the third set of experiments was performed to investigate the feasibility of periodic polarity switching of the electrodes every 2 days to overcome problems with scaling using Pt/Ir coated electrodes. Polarity switching was achieved by swapping the flows to the anode and cathode while maintaining the same direction of the current.

Following the field trials, the impact of the cathode pH and the polarity switching on the electrode lifetime was investigated using accelerated lifetime experiments. The experiments were performed (in duplicate) similar to the NACE Standard method (TMO0108-2008, Item No. 21252). To shorten the duration of the experiments the experiments were controlled galvanostatically at a current density of 100 mA cm⁻², whereas the polarity was switched every 5 minutes to accelerate the wear rate. A 0.5M Na₂SO₄ solution with a chloride concentration of 150 mg L⁻¹ (i.e., concentration often observed in sewage) was used as electrolyte. The pH was adjusted to pH 12 or 14 by the addition of NaOH.

2.3 Chemical analyses

Sulfide, sulfite, thiosulfate, sulfate and chloride concentrations were measured by Ion Chromatography (IC), using a Dionex 2010i system, according to [19]. Samples were immediately filtered using a 0.22µm syringe filter (Millipore, USA) and preserved in previously prepared Sulfide Antioxidant Buffer (SAOB) solution prior to ion chromatography analysis. SAOB solution was prepared as described earlier [20]. The conductivity and pH were measured using a hand-held meter (Cyberscan PC 300, Eutech Instruments). Elements (e.g. Sodium, Potassium, and Calcium) were measured with inductively coupled plasma optical emission spectrometry (Perkin Elmer ICP-OES Optima 7300DV, Perkin Elmer, USA). COD (range 25-1500 mg L⁻¹) was determined by means of cuvette tests (Merck, Germany). The effluent oxygen concentrations were measured using an oxygen sensor (MIQ/T2020, WTW, Germany). The oxygen concentrations to determine the coulombic efficiency for dissolved oxygen concentration were measuring a handheld dissolved oxygen meter (Pro20, YSI, Australia) placed inside a flow cell (YSI, Australia). The wear rate of the electrodes was determined by means of X-ray Fluorescence (XRF) measurements (FischerScope X-ray Xan, Germany).

3. Results and discussion

3.1 Determination of the dissolved oxygen concentration

Oxygen is generated at the electrode surface during the oxidation of water according to the following equation:



As pure oxygen is generated, higher dissolved oxygen concentrations can be obtained (i.e. ~40 mg L⁻¹) compared to air (i.e. ~8-10 mg L⁻¹). When its saturation concentration is reached, gas bubbles would be formed. Therefore, it is of major importance that the oxygen formed on the electrode surface is immediately released into the bulk solution. The achievable in-situ generated dissolved oxygen concentration depends on the amount of charge supplied to the system per volume of wastewater. At an applied flow rate of 3.6 L h⁻¹ and current densities of 5.0, 7.5 and 10 mA cm⁻², the maximum attainable oxygen concentrations are 10, 15 and 20 mg L⁻¹, respectively (in case all electrons are directed towards dissolved oxygen generation). The coulombic efficiency for dissolved oxygen generation (using a new Ta/Ir coated titanium electrode) was 60±2, 63±1 and 60±1% at current densities of 5.0, 7.5 and 10 mA cm⁻², respectively. Hence, the efficiency of in-situ oxygen generation was significantly higher than conventional oxygen injection systems with efficiencies normally below 40% [12]. The results also showed that the coulombic efficiency was not affected by the current density, implying that at all current densities oxygen reached its saturation concentration at the electrode surface. This suggests that the generation of dissolved oxygen was limited by its diffusion into the liquid and not by the kinetics of oxygen formation at the electrode surface. This is in agreement with previous studies, which showed that at low current densities gas bubbles were formed [15, 21]. During the experiments a recirculation flow of ~60 L h⁻¹ was used to provide sufficient mixing. When the recirculation flow was stopped the dissolved oxygen concentrations decreased and the coulombic efficiencies dropped below 35% (data not shown). Thus, the results indicate that the coulombic efficiency mainly depend on the mixing intensity in the current density range applied. Although the lifetime of electrodes under the conditions applied is expected to be at least several years (and thus changes over time in the efficiency of in-situ oxygen generation

are not expected), the experiments were repeated after 80 days of operation. The results show that there were no significant changes in coulombic efficiency for dissolved oxygen generation (i.e. 57 ± 2 , 62 ± 2 and $63\pm 2\%$ compared to 60 ± 2 , 63 ± 1 and $60\pm 1\%$).

3.2 Long-term performance of sulfide removal using Ta/Ir electrodes

Figure 2 shows the influent and effluent sulfide concentrations over a period of 122 days. Both reactors were operated at a current density of 10 mA cm^{-2} , except for day 68 to 80 in which a current density of 7.5 mA cm^{-2} was applied. A current density of 10 mA cm^{-2} was enough to theoretically oxidize all sulfide present to sulfate given an average sulfide concentration of 10 mg L^{-1} in the sewage. The average sulfide removal and coulombic efficiencies (based on the oxidation of sulfide to sulfate) for reactor A and B during this period were $88\pm 9\%$ and $76\pm 30\%$, respectively. In Table 1, an overview of the wastewater characteristics and final products of oxidation are presented. The table shows that in both ‘rising mains’, a mixture of sulfur species was produced, namely thiosulfate and sulfate (sulfite was negligible). This is in agreement with the findings in our previous studies [13, 14]. The total dissolved sulfur species concentration was lower than the influent. This was most likely caused by the formation of elemental sulfur as result of the oxidation of sulfide with oxygen in sewage [22]. The analytical methods used in this study were not able to directly measure sulfur in the wastewater matrix. Assuming that the difference in the measured influent and effluent inorganic sulfur species was elemental sulfur present in solid form or in soluble form as polysulfide, the average elemental sulfur produced for reactor A and B was 4.0 and 3.1 mg L^{-1} , respectively. This means that 15%, 19%, 66% and 16%, 22% and 50% were oxidized to sulfate, thiosulfate and elemental sulfur for reactor A and B, respectively.

From the above data it appears that reactor A performed better than reactor B. From day 31 till day 49 reactor B performed significantly worse with an average sulfide removal efficiency over that period of $25\pm 36\%$. This reduced performance was likely caused by a reduced HRT as the ‘rising main’ connected to reactor B was almost completely compressed due to under-pressure at the outlet. The under-pressure was probably caused by a (partial) blockage of the tubing. Both ‘rising mains’ were replaced on day 49. After replacing the ‘rising main’ the obtained sulfide removal efficiency of reactor B restored to $88\pm 12\%$ while reactor A remained at $89\pm 10\%$ (day 52 to 122). The ‘rising mains’ were used to mimic the HRT and plug flow behaviour observed in rising mains and therefore a low upflow velocity

of the system could not be avoided (i.e. $\sim 0.01 \text{ cm s}^{-1}$). Due to this low upflow velocity, a constant build-up of solids in the ‘rising mains’ was visually observed. Occasionally, for example on day 52 in reactor A and days 13, 26 and 56 in reactor B, this most likely caused a reduction in the sulfide removal efficiency due to an increase in oxygen consumption for microbial oxidation of organics due to this biomass build-up. To check this hypothesis, samples were taken before and after flushing of the system. Indeed, IC analyses showed a significant lower sulfide removal (or even slight increase in sulfide concentration due to SRB activity) before flushing, confirming our hypothesis (data not shown). A build-up of biomass in a full scale application would not occur since the upflow velocity normally applied in rising mains of sewer networks (i.e. $\sim 0.8 \text{ m s}^{-1}$) is sufficient to prevent sedimentation of any formed biomass or other particles.

Table 1. Characteristics of the sewage from the Elanora rising main (Gold Coast, Australia).

parameter	Influent	Effluent rising main A	Effluent rising main B
chloride (mg L^{-1})	395 \pm 80	329 \pm 97	339 \pm 108
sulfide-S (mg L^{-1})	9.2 \pm 1.2	1.9 \pm 2.0	2.7 \pm 2.7
sulfate-S (mg L^{-1})	14.3 \pm 4.7	15.2 \pm 3.0	15.3 \pm 6.3
thiosulfate (mg L^{-1})	0.9 \pm 0.6	2.4 \pm 1.5	2.6 \pm 1.6
sulfite (mg L^{-1})	0.2 \pm 0.2	0.2 \pm 0.2	0.2 \pm 0.2
sulfur (mg L^{-1}) ^{a)}	-	4.05	3.06
COD _{soluble} (mg L^{-1})	189 \pm 50	182 \pm 55	183 \pm 46
pH	7.0 \pm 0.10	6.8 \pm 0.1	6.8 \pm 0.2
conductivity (mS cm^{-1})	1.64 \pm 0.2	1.52 \pm 0.1	1.51 \pm 0.1
sodium (mg L^{-1})	318 \pm 108	n.d.	n.d.
calcium (mg L^{-1})	38 \pm 3	n.d.	n.d.
magnesium (mg L^{-1})	33 \pm 16	n.d.	n.d.
potassium (mg L^{-1})	26 \pm 6	n.d.	n.d.

a) The difference in the influent sulfide-S and effluent sulfide-S (i.e. oxidized to $\text{SO}_3\text{-S}$, $\text{S}_2\text{O}_3\text{-S}$ and $\text{SO}_4\text{-S}$) was assumed to be elemental sulfur present in solid form or in soluble form as polysulfide.

After 80 days of operation the Ta/Ir coated titanium anode of reactor B was replaced by a Pt/Ir coated titanium anode. Figure 2 shows that similar sulfide removal efficiencies were obtained, which is in agreement with our previous work in which we showed that the sulfide

removal efficiency is not significantly affected by the electrode material used due to the indirect nature of most of the oxidation as discussed in the introduction section.

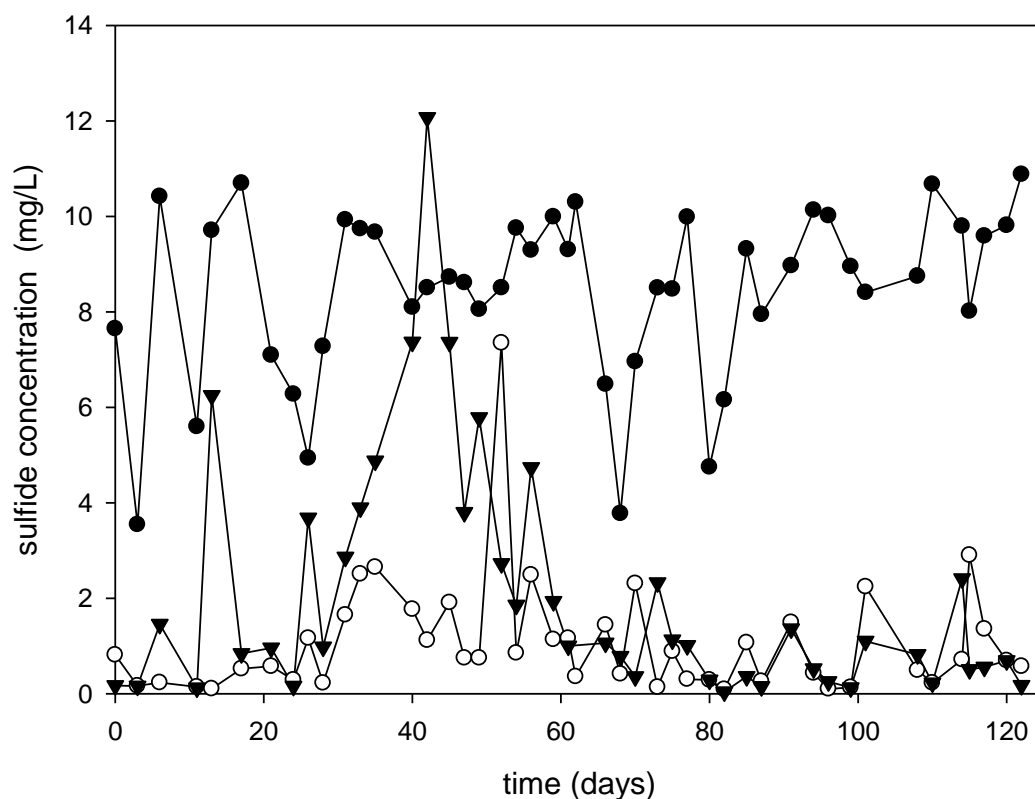


Figure 2. (A) Sulfide-S influent (●) and effluents concentrations for reactor 1 (○) and reactor 2 (▼) over a period of 122 days.

3.3 Impact of cell operation on required energy input

Figure 3 shows the anode and cathode potentials of the two reactors over the second set of field trials over 80 days. During the course of the experiments the anode potentials were stable (1.6 ± 0.1 V and 1.6 ± 0.1 V versus SHE for reactor A and B). Only from day 60 to 65 (reactor B) and day 72-77 (reactor A) the anode potentials fluctuated significantly due to malfunctioning reference electrodes. After replacing the reference electrodes the anode potentials returned to their original values.

On the other hand, the cathode potentials measured relative to the reference electrode in the anode significantly fluctuated over time from approximately -2.5 V down to approximately -12 V. We hypothesised that this was associated with an increase in membrane resistance due to membrane fouling caused by precipitation of calcium and magnesium. To confirm this hypothesis, in a second stage, a reference electrode was placed inside the

cathode chamber of reactor B, which showed stable cathode potentials (see Figure 4). Hence, the increase in cell voltage was likely related to an increase in membrane resistance. The precipitation accumulated on the membrane surface was scraped off and analysed to determine the presence of calcium and magnesium. Indeed, analysis confirmed the presence of calcium ($35 \pm 0.1\%$ $n=2$) and magnesium ($65 \pm 0.1\%$ $n=2$). Periodic cleaning (i.e. ~once per week) of the cathode compartment with a 0.05 M HCl solution was successful in removing the scaling from the electrode and membrane surface. The scaling on the membrane surface was mainly observed in the vicinity of the cathode surface. In addition to periodic cleaning with HCl, the cathode potentials also returned to their original values when there was a blockage in the anode feed line (for example on day 6, 20). As result of a blockage, there was no feed to the anode chamber, while protons were generated continuously during the oxidation of water to oxygen. Hence, an acid solution was generated in-situ in the anode compartment, during which protons were likely transported through the membrane to the cathode lowering the pH in the membrane and its vicinity. This pH decrease removed the scaling inside the membrane. Consequently, the ohmic resistance over the membrane dropped and the overall cell potential decreased.

At some stages, the decrease in cathode potential was also caused by operational constraints. On day 5, 15 and 28 the cathode solution accidentally ran out due to issues with the feed pump and valves. Occasionally a blockage occurred in the effluent tube of the anode compartment (day 10, 18) caused by the small dimensions of the connectors. The blockage created a significant pressure build up as the peristaltic pumps were still running. As a result, the membrane was pushed towards the cathode chamber pushing the cathode away (even though they were fixed), thereby increasing the distance between the anode and the cathode (up to 1 cm difference). The theoretical increase in ohmic resistance between the anode and cathode at a current density of 10 mA cm^{-2} and a conductivity of 1.5 mS cm^{-1} is $\sim 0.7 \text{ V}$ per mm distance [23]. Hence, this had a significant impact on the required cell voltage. From day 38 to 57 the data acquisition unit (34970A Data Acquisition Unit, Agilent Technologies, USA) occasionally stopped working and was therefore replaced. Consequently, no data was recorded during these periods (see Figure 3). These are issues difficult to avoid when working on site with laboratory-scale systems.

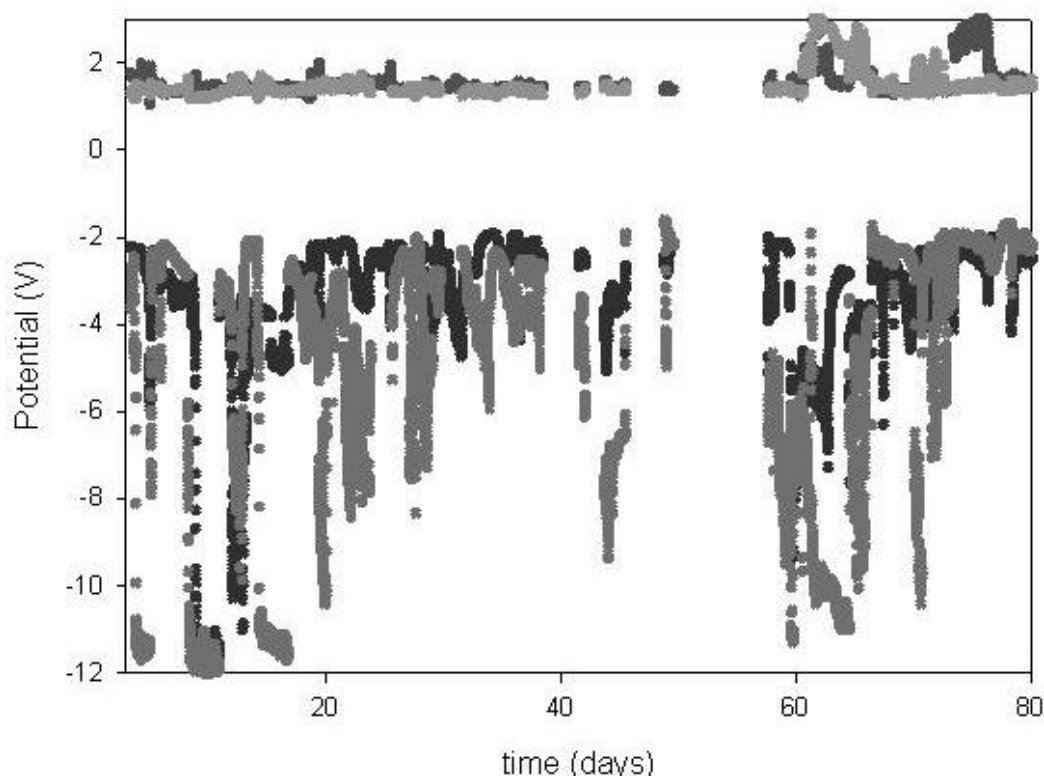


Figure 3. Anode and cathode potentials (including ohmic losses) of reactor A (black) and reactor B (grey) over a period of 80 days.

It was previously shown that switching electrode polarity every four hours was effective to remove membrane scaling using Pt/Ir coated titanium electrodes [16]. Such a frequent polarity reversal could not be tested in the field as the system used did not allow the automatic switch, and physical distance between the field location and our laboratory did not allow frequent manual switching. A less frequent switching would be preferred from an operational point of view anyway, as it may extend the electrode lifetime (personal communication Pieter Hack, Magneto Special Anodes B.V.). Therefore, in this study we investigated the feasibility of switching the polarity every 2 days. To do so, after day 80, both electrodes of reactor B were changed to Pt/Ir electrodes. From day 80 reactor A was operated as before, while in reactor B the polarity was switched every 2 days as explained in section 2.2.

To accurately assess the feasibility of polarity switching to overcome scaling, blockages of the anode should be avoided at all times as scaling would be dissolved by in-situ generated acid, as previously discussed. Therefore, during this period, the cells were operated at a current of 1 mA during the weekends (and public holidays) as the site was inaccessible at such times. Figure 4 shows the profiles of the cathode potential including ohmic losses of

reactor A (without polarity switching) and the cathode potentials with and without ohmic losses of reactor B (with polarity switching) over a period of 34 days. There was a clear increasing trend for the cathode potentials after switching the polarity of reactor B. However, a much more frequent switching of the polarity would be required to minimize the required cell voltage due to the fast increase in ohmic resistance. As a result of the rapid scaling, switching the polarity every two days resulted in only a slight, non-significant decrease in required energy input with average cathode potentials of -8.4 ± 1.4 and -7.3 ± 1.4 for reactor A and B, respectively. It can be seen that after the first weekend period the cathode potentials of reactor A also increased (slightly). This was most likely caused by the fact that the pH in the cathode compartment decreased to neutral levels as only a current of 1 mA was applied over the weekend, while maintaining a continuous flow. As a result of this, the scaling likely slowly dissolved or was washed off over the weekend. After this period, the flow to the cathode compartments was stopped over the weekend, leading to unchanged pH values in the cathode and a disappearance of the effect on cathode A.

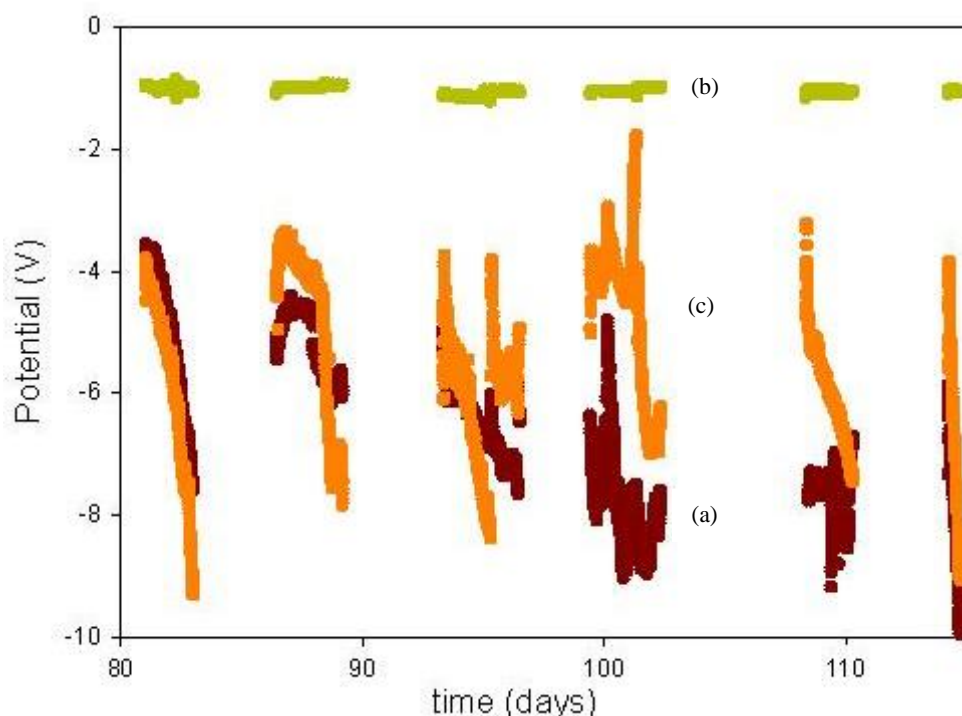


Figure 4. Cathode potentials including ohmic losses (brown (a)) of reactor A (regular operation) and the cathode (green (b)) and cathode potentials including ohmic losses (orange (c)) for reactor B (polarity switching) over a period of 34 days.

3.4 Determination of the electrode lifetime

Polarity switching to overcome scaling issues can have a significant impact on the electrode life-time [17, 24, 25]. Moreover, elevated pH values as obtained in the cathode compartment may also negatively affect the electrode lifetime. Therefore, accelerated lifetime experiments similar to the NACE Standard method (TMO0108-2008, Item No. 21252) were performed at pH levels of 12 and 14, respectively. These tests are widely used to predict the lifetime under realistic conditions [26]. The end of the electrode service life was determined as the time where the cell voltage increased significantly (i.e. > 5 Volt) or by the wear rate (i.e. dissolution of the catalytic coating in gram coating per MAh of operation), depending on the experiment performed. To shorten the duration of the experiments, the current density applied was 100 mA cm^{-2} , whereas the frequency of polarity switching was increased to every 5 minutes. To then extrapolate the obtained results to a practical situation, that is, a current density of 10 mA cm^{-2} and polarity switching every 4-8 hours, a correction factor has to be applied. Based on practical experience (personal communication Vidjay Birdja, Magneto Special Anodes B.V., Schiedam, the Netherlands) a correction factor of 5-8 can be considered. In Figure 5A and 5B the results of the accelerated lifetime experiments at pH 12 and 14 are presented.

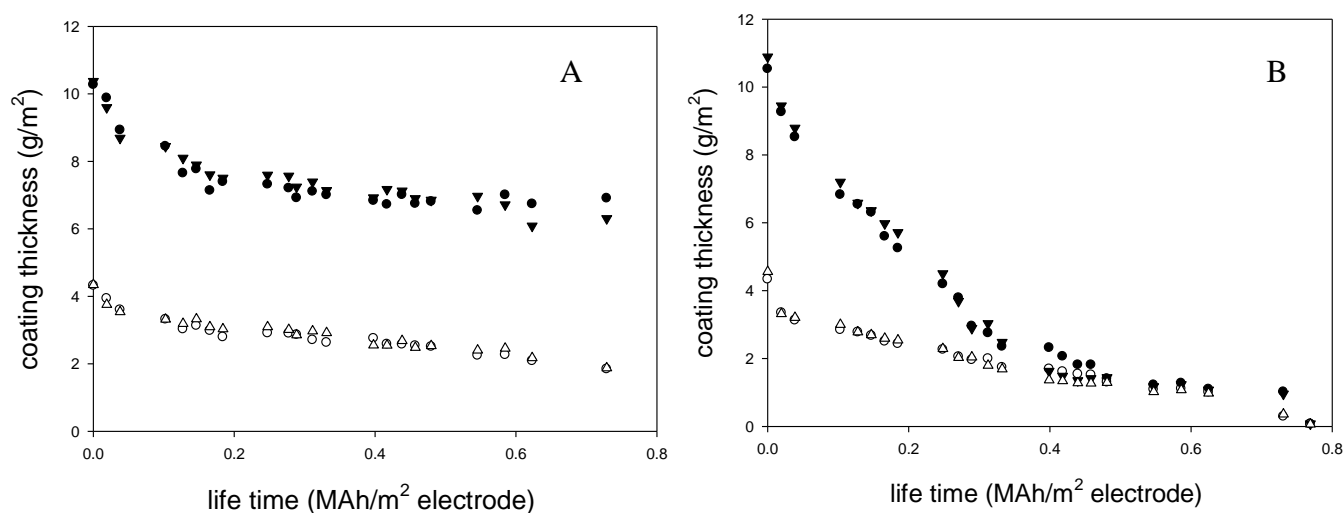


Figure 5. The wear rate (gram MAh m⁻² electrode) at pH=12 (A) and pH=14 (B) during accelerated lifetime experiments.

The results show that the electrode lifetime is significantly affected by the pH. The expected lifetime of the Pt/Ir electrode at pH 14 is approximately 6.0 ± 1.9 years (depending on the correction factor), whereas at pH 12 the wear rate of the coating is very low (i.e. coating

thickness is only slightly reduced) and thus electrode lifetimes over 30 years can be expected. In a practical situation, a divided reactor is used in which the electrodes are only exposed to a high pH in the cathode compartment, which is 50% of the time. The other period at neutral to low pH values is expected to further increase the electrode lifetime. However, in a practical situation, also the presence of organics in sewage and mechanical wear (i.e., due to physical shear/friction of solids such as sand on the electrode surface) could have a negative impact on the electrode lifetime.

3.5 Implications for practice

In this study, we investigated the long-term performance of electrochemical sulfide removal under real sewer conditions. Sulfide could be removed to concentrations below 1 mg L^{-1} at average sulfide removal efficiencies above 80%, after a residence time more than 1 hour through a simulated rising main. Such a removal is an excellent outcome from a practical perspective. The cathode was operated in a continuous mode with a short HRT (3.3 minutes) similar to the anode compartment as discussed in section 3.3. In a practical situation, sewage is passed through the anode with the same short HRT continuously generating oxygen, while at the cathode a small volume of clean water without any buffer is constantly recirculated. As such, a strong caustic solution can be produced in the cathode over a period of days without inducing significant changes in pH in sewage. This caustic can then be dosed to the sewer to create a peak pH for a short period to deactivate the SRB in the biofilms of the sewer pipes. This would allow for a much more compact and very cost effective system as previously described [16]. When producing a concentrated caustic solution, higher pH values will be obtained, which may result in a more severe scaling. However, it has to be highlighted that in this study tap water containing about 50 mg L^{-1} calcium and magnesium was used to prepare the cathode solution. Thus, there was a continuing supply of these key scaling ions to the cathode which could be avoided in many applications.

Polarity switching every 2 days is not sufficient to overcome scaling and thereby reducing the energy requirements of the system, whereas during laboratory scale experiments we showed that switching the polarity every 4 hours was effective [16]. The results also showed that acid can be generated in-situ in the anode by operating the cell without any flow (in our case accidentally due to blockages). Hence, this acid can subsequently be pumped into the cathode chamber to dissolve the scaling as an alternative for frequent polarity switching. This would preferably be done during the night, during which low sewer flow occurs. This would

allow for a system in which cost effective cathode materials such as stainless steel or nickel can be used due to the absence of polarity switching, reducing the capital cost. Long term trials at larger scale in which either the polarity is switched every 4-8 hours (automatically) or acid is generated in-situ are necessary to establish which of the options would be better under stable conditions.

The accelerated lifetime experiments showed that the pH had a significant impact on the electrode lifetime. In addition, the presence of organics in sewage and mechanical wear could have a negative impact, which has not yet been established. Hence, further research is warranted to determine the optimum pH for the cathode compartment to ensure a sufficient electrode service life.

For the successful application of an electrochemical system in sewers, several process and engineering issues have to be solved. The most important engineering considerations are the prevention of ragging, blockage of the electrochemical system and the use of valves. Other engineering considerations that have to be taken into account are the prevention of particle and biomass settling and accumulation, precipitation of inorganics, biofouling of the membrane surface, diurnal flow variations and minimizing electrode losses. All parts of the electrochemical cell need to be constructed as such that it will not have any bars, protrusions, sharp and uneven parts so hair and rags cannot rap around. The design of the electrochemical cell must be such that large obstacles can freely flow through the sewer pipe and the electrochemical reactor. Prevention of particle and biomass accumulation can be avoided by applying a sufficient upflow velocity.

Large temporal as well as spatial variations in the wastewater composition (i.e. sulfide, organics and sulfate concentrations) can be observed in sewer systems. In this study, significant fluctuations in sulfide influent concentrations, ranging between ~ 3 to 11 mg L^{-1} were observed. Hence, these fluctuations can have a significant impact on the required energy requirement. Online sulfide sensors developed recently [27] can be used for the design of online control systems.

4. Conclusions

Sulfide can be efficiently removed from domestic wastewater using an electrochemical cell under realistic sewer conditions to levels below 1 mg L^{-1} . The coulombic efficiency for dissolved oxygen generation was $\sim 60\%$ and not significantly affected by the current density. Scaling of inorganics in the cathode compartment was observed resulting in an increase in

cell potentials and thus energy requirements over time. The cathode potentials returned to their original values after polarity switching. The rate at which the ohmic resistance increased was such that polarity switching every two days was not sufficient to reduce the required energy input. The expected electrode lifetime under polarity switching at pH 14 is expected to be at least 6.0 ± 1.9 years and can significantly be extended by using a lower pH. The results suggest that electrochemical sulfide abatement is a promising technique for the prevention of sewer corrosion.

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APPENDIX E

Summary of thesis report ‘Efficiency of Cathodic Electrosynthesis of Hydrogen Peroxide at Carbon Catalysed Gas Diffusion Electrodes’

1. Objective of the study

The main objective of this study was the development of inexpensive carbon based gas diffusion electrodes (GDEs) for the efficient cathodic generation of hydrogen peroxide.

2. Methodology

2.1 Electrochemical cell

The electrochemical cell consisted of two parallel Perspex frames (internal dimensions 14 x 12 x 2 cm) that were separated by a cation exchange membrane (Ultrex, Membranes International Inc., USA). Both empty volumes of anode and cathode chambers were 336 mL. A Perspex plate was used to isolate the anode chamber from outside and a mesh shaped Ta/IrOx coated titanium electrode (Magneto Anodes BV, The Netherlands) with a projected surface area of 100 cm² was used in the anode chamber. Carbon fibre papers (TGP-H-030, Toray Industries, Inc., USA) with different catalytic coatings were used as the cathode electrode and separator of the cathode chamber and the outside. A 225 cm² surface area nickel current collector (S37110/4Ni 23-284, Dexmet Corporation, USA) was contacted with a GDE. An Ag/AgCl reference electrode (RE-5B, Bio Analytical, USA) was used in the cathode chamber and its potential was estimated at +197 mV versus standard hydrogen electrode (SHE). In all experiments, the electrochemical cell was controlled galvanostatically by a VMP3 potentiostat (Princeton Applied Research, USA). A multichannel data acquisition unit (34970A Data Acquisition Unit, Agilent Technologies, USA) was used to record both anode and cathode potential in 60 second intervals. All electrode potentials reported here were adjusted vs. SHE.

2.2 Fabrication of gas diffusion electrodes

Although the carbon base materials used to make the GDEs were claimed to be waterproof, leakages of GDEs in all carbon papers occurred. Therefore, additional PTFE layers were needed to prevent the GDEs from leaking. PTFE was also used as binder for the catalytic layers. One PTFE layer consisted of 1.0 mL PTFE solution (60% polytetrafluoroethylene, Aldrich) and 0.2 mL demineralised water, painted on the carbon base material by brushing and air-dried for at least 2 hours and subsequently heated for 20 minutes at 370 °C. Vapor grown carbon fibre (VGCF, 13 m² g⁻¹, Showa Denko Co., Japan), activated carbon (Acticarb PS1000, Activated Carbon Technologies PTY LTD, Australia) and Vulcan XC72 carbon black (VULCAN XC72, Cabot Corporation, USA), or a mixture of these materials, were used as the catalytic layer. One catalytic layer consisted of 225 mg carbon mixture, 1.8 mL 60% PTFE solution and 1.8 mL demineralised water, painted on the solution side and air-dried for more than 2 hours. Similar to the PTFE method above, this air-dried carbon base was heated for 20 minutes at 370 °C. An overview of the different catalytic compositions used is presented in Table E1.

Table E1. Different mixtures of catalytic layers used for the fabrication of GDEs.

Carbon base material	Number of PTFE layers ^{a)}	GDE Number	Catalytic mixtures ^{b)}		
			VGCF	AC	XC 72
Toray carbon fibre paper TGP-H-030	3	A-Blank test	-	-	-
		A-1	100%	-	-
		A-2	-	100%	-
		A-3	-	-	100%
		A-4	50%	50%	-
		A-5	75%	25%	-
		A-6	50%	-	50%
		A-7	75%	-	25%
		A-8	25%	-	75%
		A-9	33%	33%	33%
VGCF: Vapor grown carbon fibre; AC: Activated carbon; XC72: Vulcan XC 72 carbon black					
a): For each PTFE layer: 0.2 mL demineralised water and 1.0 mL 60% PTFE solution					
b): A total amount of 225 mg carbon mixture, 1.8 mL 60% PTFE solution and 1.8 mL demineralised water was used					

2.3 Experimental procedures

Short-term (8 hours) experiments were performed with 10 different carbon gas diffusion electrodes (see Table E1). During these experiments, the electrochemical cell was galvanostatically operated at a fixed current of 100 mA for 8 hours. Prior to each run, all the tubing and bottles were rinsed 3 times with demineralised water. A NaHCO₃ solution (12.5 g

L⁻¹) was used in the anode compartment, whereas a NaCl solution (5 g L⁻¹) was used in the cathode compartment. The anode solution was recirculated over a 2 L external buffer vessel at a flow rate of 3.8 L hr⁻¹, whereas the cathode solution was recirculated over a 0.5 L buffer vessel at a flow rate of 3.8 L hr⁻¹. Samples were taken every 2 hours (t= 0, 2, 4, 6 and 8 hour) for analysis of hydrogen peroxide. The hydrogen peroxide concentration was measured by using the vanadate method [1].

These experiments aimed to determine the impact of the catalytic layer composition on the coulombic efficiency of hydrogen peroxide generation. In addition, long-term experiments were performed to investigate the long-term H₂O₂ generation performance. During these experiments, the anode solution was replaced every 2 days, whereas samples were taken approximately every 24 hours.

3. Results and discussion

Figure E1 shows the results of the short term experiments using 10 different carbon gas diffusion electrodes. The results show that hydrogen peroxide could be generated at coulombic efficiencies up to 90% using VGCF, Vulcan XC72 or a mixture of these compounds.

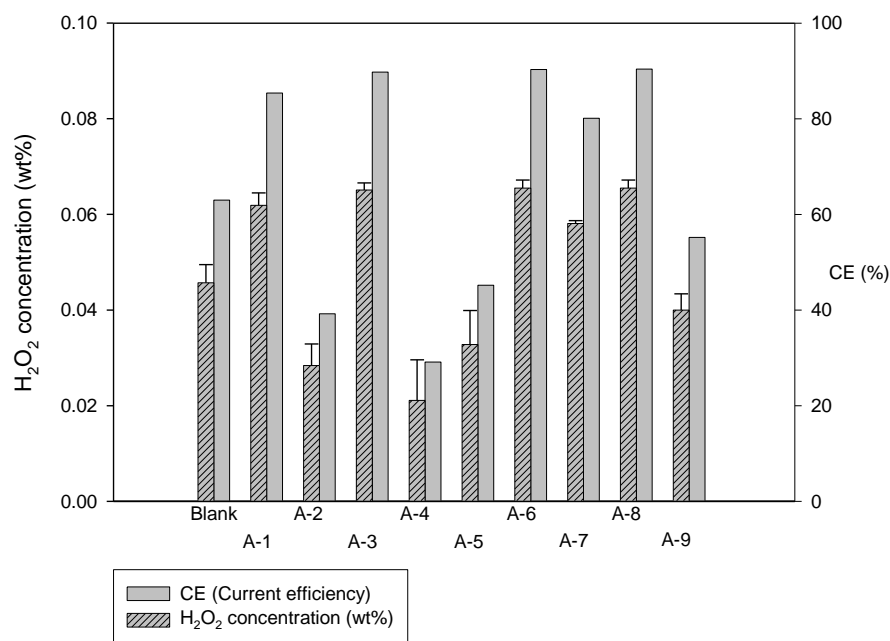


Figure E1. Coulombic efficiency for hydrogen peroxide generation (%) and hydrogen peroxide concentration (wt %).

In a second stage, several long term experiments were performed using either VCGF or Vulcan XC72 to determine the long-term performance and maximum attainable hydrogen peroxide generation. In all experiments, initially the hydrogen peroxide concentration increased, then flattened off and subsequently decreased. Moreover, the catalytic activity of the GDEs could not be recovered by cleaning the electrode. An example of such a profile obtained during a long-term experiment is shown in Figure E2. Based on the results we hypothesised that the hydrogen peroxide reacted with NaOH to form NaOOH or $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ blocking the oxygen diffusion of the GDE [2].

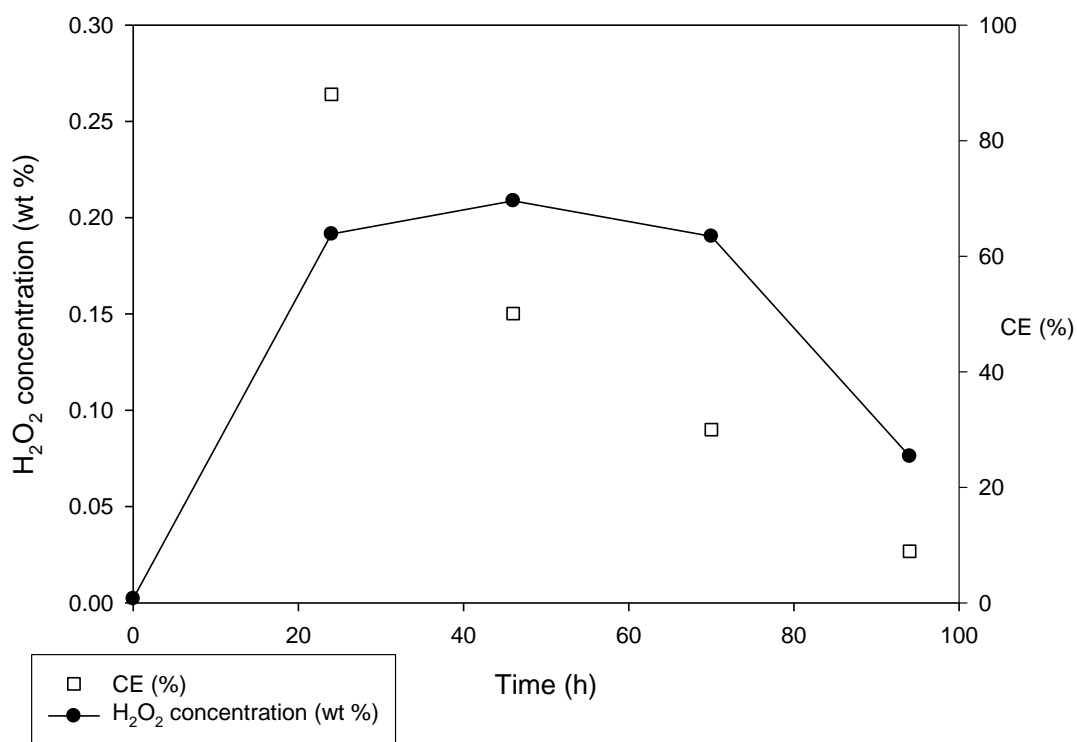


Figure E2. Example of long-term performance of hydrogen peroxide generation using VGCF as catalyst material.

4. Conclusions

A long term stable operation for the cathodic generation of hydrogen peroxide could not be achieved, which was most likely caused by blockage of the GDE by NaOOH or $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$. Hence, the use of GDE does not seem suitable for sewer applications.

References

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