



**DETAILED TECHNICAL
SUBPROJECT RESEARCH REPORT**

ON

**ARC CORROSION & ODOUR
LINKAGE PROJECT
LP0882016**

Sub-project Title	<i>Electrochemical abatement of sulfide in sewer systems</i>		
Sub-project No.	<i>SP7</i>	Date	21-02-2011



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1.0 SUMMARY OF RESEARCH ACTIVITIES TO DATE

1.1 Activities Completed

1.1.1 Activities Completed Previously

The activities completed in the previous period were:

Anodic half cell tests	
<p>Aim:</p> <ul style="list-style-type: none"> - To investigate the indirect electrochemical removal of sulfide through in-situ oxygen or radical (Cl[•], OH[•]) formation to elemental sulfur, thiosulfate or sulfate from domestic wastewater as a function of the anode material. The tested anode materials were Ta/Ir, Ru/Ir, Pt/Ir, SnO₂ and PbO₂ coated titanium electrodes. - To investigate the impact of chloride on the kinetics of sulfide oxidation and the overall cell potential (i.e. required energy input) using Ru/Ir and Ta/Ir coated titanium. 	<p>Outcome:</p> <ul style="list-style-type: none"> - The experiments for indirect anodic sulfide oxidation by means of in-situ oxygen and/or radical generation at a current density of 100 A m⁻² using domestic wastewater have been completed. - The experiments at elevated chloride concentrations (i.e. 1100mg L⁻¹) at a current density of 100 A m⁻² using domestic wastewater have been completed. - 'Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities' was submitted to Water Research.
Cathodic half cell tests	
<p>Aim:</p> <ul style="list-style-type: none"> - To investigate the electrochemical reduction of oxygen at the cathode chamber with hydrogen peroxide as a product. 	<p>Outcomes:</p> <ul style="list-style-type: none"> - Experiments for the in-situ cathodic generation of hydrogen peroxide using gas diffusion electrodes have been performed (outside scope of SP7). This is still work in progress and will feed into SP7 later.
On site reactor operation	
<p>Aim:</p> <ul style="list-style-type: none"> - To investigate the feasibility of sulfide removal from sewer systems by means of indirect anodic oxidation of sulfide through in-situ generated oxygen using two laboratory scale electrochemical cells during long-term experiments (i.e. continuous operation for at least 4 weeks) 	<p>Outcomes:</p> <ul style="list-style-type: none"> - The laboratory scale reactors (and all other equipment) have successfully been installed. - Start-up of the systems has been delayed as a result of power shutdowns (see below).



1.1.2 Activities Completed This Reporting Period

Anodic half cell tests	
<p>Aim:</p> <ul style="list-style-type: none"> - The experiments for indirect anodic sulfide oxidation by means of in-situ oxygen and/or radical generation at a current density of 100 A m⁻² using domestic wastewater at different chloride concentrations were finished in the previous period. 	<p>Outcomes:</p> <ul style="list-style-type: none"> - The results have been summarized in a scientific paper ‘Electrochemical sulfide oxidation from domestic wastewater using mixed metal coated titanium electrodes’ (submitted to Journal of Hazardous Materials) - ‘Electrochemical sulfide removal from synthetic and real domestic wastewater at high current densities’ was accepted in Water Research.
Cathodic half cell tests	
<p>Aim:</p> <ul style="list-style-type: none"> - To investigate the cathodic generation of a concentrated caustic soda solution coupled to anodic oxygen generation from domestic wastewater using Pt/Ir coated titanium electrodes. 	<p>Outcomes:</p> <ul style="list-style-type: none"> - Electrochemical reactors and Pt/Ir electrodes have been ordered and received. - The experimental setup (i.e. laboratory scale reactors and all other equipment) have been successfully installed. - First set of experiments have been performed at a current density of 100 A m⁻², the results of which will be reported later.
On site reactor operation	
<p>Aim:</p> <ul style="list-style-type: none"> - To investigate the feasibility of sulfide removal from sewer systems by means of indirect anodic oxidation of sulfide through in-situ generated oxygen using two electrochemical cells during long-term experiments. 	<p>Outcomes:</p> <ul style="list-style-type: none"> - The experiments have been running for more than 82 days at a current density of 100 A m⁻² using Ta/Ir coated titanium electrodes. - The experiments have been postponed for one month during the Christmas period, heavy rain (i.e. hardly any sulfide present in the wastewater) and the flood.

1.2 Activities In Progress

1. Continuation of the onsite experiments with two laboratory scale reactors to determine the feasibility of sulfide removal from sewer systems by means of indirect anodic oxidation of sulfide through in-situ generated oxygen. The current focus of the experiments is the investigate the feasibility of polarity switching to overcome scaling issues.



The electrode materials used are Ta/Ir and stainless steel cathode in reactor 1 (no polarity switching) and Pt/Ir in reactor 2 (with polarity switching). In order to assess the feasibility of polarity switching as a means to overcome scaling, the anode/cathode are switched twice a week. The anode, cathode and overall cell potentials are monitored every 5 minutes using a data acquisition unit. Sulfide influent and effluent concentrations are taken 3-5 times a week.

2. Continuation of the laboratory scale experiments to determine the feasibility of cathodic caustic generation for pH shock-loading to inactivate/kill the sulfate-reducing bacteria present in the biofilm of the sewer pipes. The electrode material used in both the anode and cathode chamber is Pt/Ir coated titanium. Experiments will be performed at a current density of 100 A m^{-2} , whereas the anode and cathode are regularly switched (anode becomes cathode and cathode becomes anode and vice versa) to avoid scaling issues.

1.3 Deviations from Agreed Research Plan

- The ordered boron-doped diamond (BDD) electrode still has not arrived. BDD is more interesting from a scientific point of view than for a practical application due to its high cost per projected surface area. Hence, it is decided to leave this out of the experimental work of SP 7. Other packages will still proceed as planned.
- The onsite experiments will last longer (i.e 4 to 6 weeks) than expected due to the Queensland floods and heavy precipitation during and after the Christmas period.

2.0 On-site experiments

Aim: to determine the long term performance of electrochemical sulfide oxidation from domestic wastewater by means of in-situ oxygen generation.

2.1 Experimental Methodology

2.1.1 Lab Test Set-up & Procedures

The experimental setup used for the field trials was previously described in detail in the progress report of August 2010 (TAC detailed Research report August 2010). The adjustments made to the original experimental setup are detailed below:

- The cathode compartment of the two-chambered electrochemical cell consists of a parallel Perspex frame with internal dimensions of $19.5 \times 4.8 \times 2.0 \text{ cm}^3$ instead of $19.5 \times 4.8 \times 1.2 \text{ cm}^3$ to create a cathode volume of approximately 200 mL.
- Initially, both reactors consisted of a mesh shaped Ta/Ir coated titanium electrode (Magneto Anodes BV, Schiedam, The Netherlands) as anode material and stainless steel fine mesh as cathode material for 82 days. After that, the anode and cathode materials of one reactor were replaced by Pt/Ir coated titanium electrodes.
- The hydraulic retention time (HRT) of the 'rising main' is 1 hour and 20 minutes instead of 1 hour.
- The 'rising mains' are flushed on a weekly basis to prevent accumulation of biomass and other particles. The accumulation of biomass and particles is the result of the low up-flow velocity in the 'rising mains'. A low up-flow velocity is applied because the diameter of the tubing of the rising mains would otherwise be too small, leading to (a) a very high surface-



to-volume ratio of the rising main (i.e. much more biofilm would be observed than in a full scale application; and (b) the length of the tubing being too long. In a practical situation, the normal flow velocity used in the rising main would be able to prevent the accumulation of biomass and particles.

- Additional experiments are currently being performed in the laboratory of the AWMC to investigate the stability of the used electrodes based on the efficiency to generate dissolved oxygen. Experiments will be performed using (a) a brand new electrode, (b) an electrode after 82 days of operation and (c) an electrode at the end of the on site experiments.

2.1.2 Analytical Methods

The analytical methods used for the laboratory scale experiments for the determination of aqueous sulfur species (i.e. sulfide, sulfite, thiosulfate, sulfate), chloride, COD, acetate, pH and conductivity was previously described in detail in the progress report of August 2009 (TAC progress report August 2009). In addition, the effluent oxygen concentrations were measured using an oxygen sensor (MIQ/T2020, WTW, Germany).

2.2 Results and discussion

The field trials were performed in duplicates (i.e. two identical reactors) and divided into two different sets of experiments. In the first set of experiments, the feasibility and stability of the electrochemical process in terms of sulfide removal efficiency and required energy input was investigated using Ta/Ir coated electrodes at a current density of 75-100 A m⁻² projected electrode surface area for 68 days. In the second set, the feasibility of Pt/Ir coated electrodes and polarity switching as a means to overcome scaling issues were investigated.

Figure 2.1 shows the sulfide influent and effluent concentrations over a period of 82 days. The first 68 days of the experimental run both reactors operated at a current density of 100 A m⁻². This current density was enough to theoretically oxidize all the available sulfide to sulfate (at an influent sulfide concentration of 10 mg L⁻¹). During day 68 to 82 a current density of 75 A m⁻² was applied to observe its effects on the sulfide oxidation efficiency.

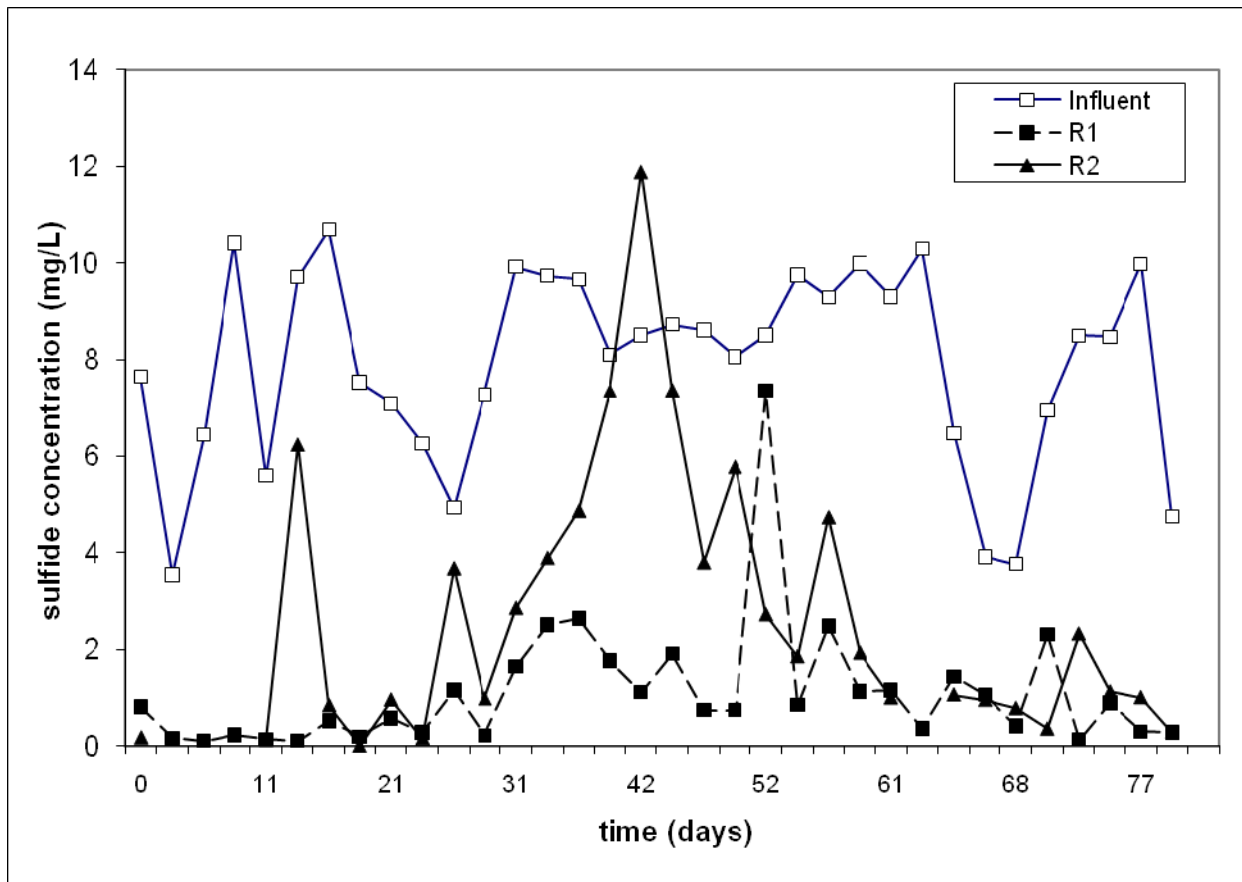


Figure 2.1. sulfide influent concentrations (\square) and sulphide effluent concentrations for reactor A (\blacksquare) and reactor B (\blacktriangle).

- The average removal efficiencies for reactors A and B during this period were $85\pm 17\%$ and $70\pm 24\%$, respectively. On average, reactor A performed slightly 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 $42\pm 19\%$. The latter was caused by a decrease of the HRT of the system since the tubing of the ‘rising main’ was almost completely compressed due to under pressure of the system (visually observed). This under pressure was probably caused by a (partial) blockage of the tubing. Both ‘rising mains’ were replaced on day 49. Figure 2 shows that after replacement of the ‘rising main’ the sulfide removal efficiency of reactor B increased to approximately the original values of $75\pm 13\%$.
- On day 52, samples ($n=6$) were taken in the absence of the ‘rising main’ to confirm that the sulfide removal was predominantly removed by in-situ generated oxygen instead of direct oxidation on the electrode surface area. The sulfide removal by direct oxidation appeared to be insignificant (data not shown).
- On some days, for example, day 52 for reactor 1 and days 13 and 26 for reactor 2, the reactors performed significantly worse in terms of sulfide removal. These unexpected values are most likely a result of the significant build up of biomass in the ‘rising mains’ (visually observed) due to the low up-flow velocity.
- The sulfide removal efficiency during days 68 to 82 were $89\pm 12\%$ and $78\pm 18\%$ for reactors A and B, respectively, which suggests that the system can be further optimized with respect to the amount of energy input per kg of sulfide-S removed.

Figure 2.2 shows the profile of the anode and cathode potentials for Reactor A and B over a period of 82 days.

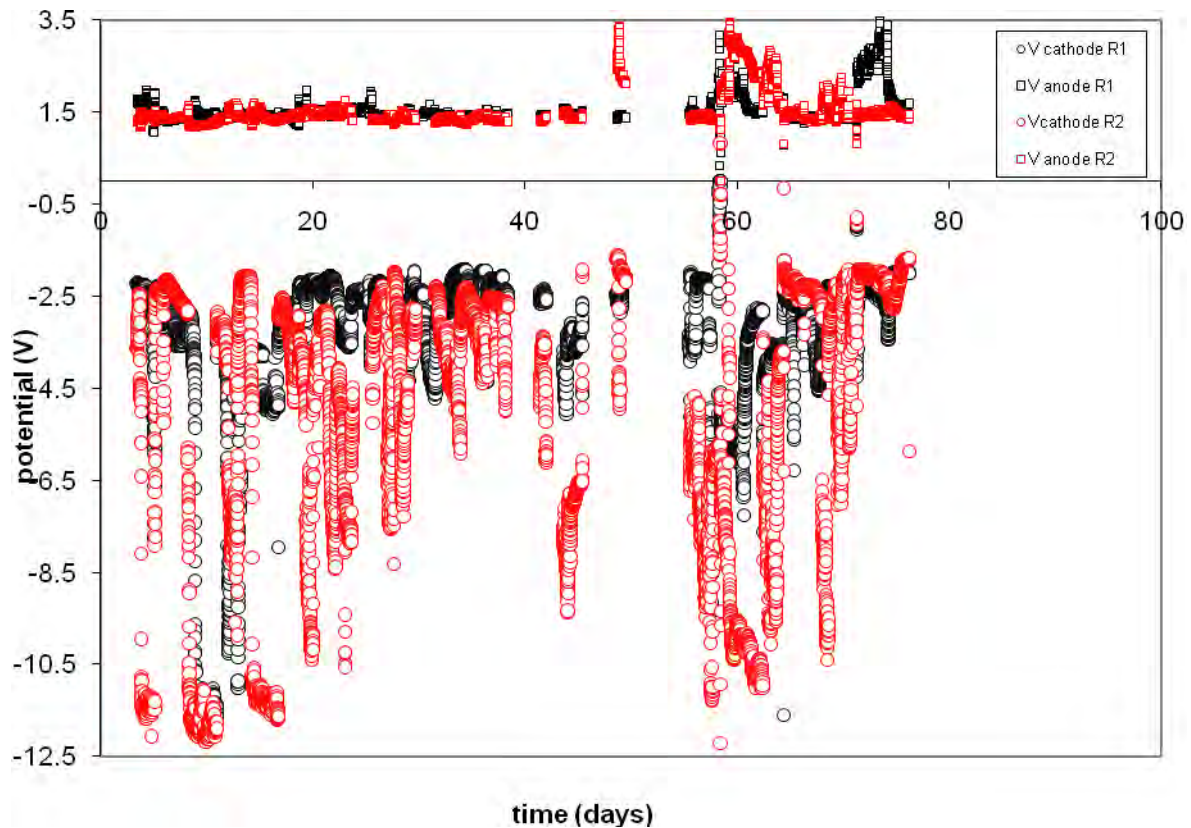


Figure 2.2 Anode and cathode potentials of reactor A and B in Volts over a period of 82 days.

- Over the course of the experiments the anode potentials were (fairly) stable at potentials of 1.5V versus standard hydrogen. Only at day 60 to day 75 the anode potentials of both reactors fluctuated significantly. It appeared that the reference electrodes were not working properly anymore. After replacing the reference electrode the anode potentials returned to their original values.
- The cathode potentials decreased over time from -2.5V up to -12V. The latter was in some occasions caused by running out of cathode solution, but mainly caused by scaling of the electrode and the membrane surface (i.e. scaling was visually observed on both the electrode and membrane surface).
- The cathode potentials returned to their original values (i.e. approximately -2.5 to -3Volt) after cleaning the cathode chamber with a 0.01M hydrochloric acid solution.

The oxygen concentrations at the end of the rising main were below 1 mg/L. An example of the oxygen concentration for reactor B is given in Figure 2.3.

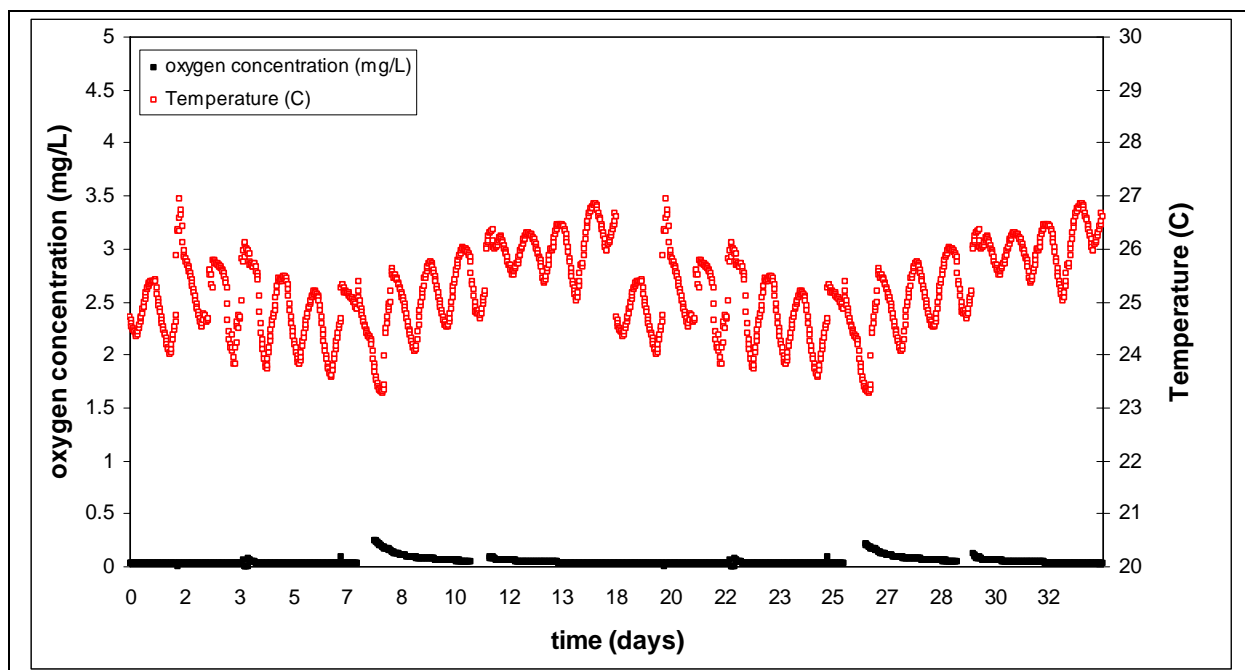


Figure 2.3 oxygen concentrations at the end of the rising main of reactor B.

2.4 Conclusions

- Sulfide can be removed to values under the target value of 1 mg L^{-1} using an electrochemical cell under real sewer conditions.
- The average obtained sulfide removal efficiency was $85 \pm 17\%$ and $75 \pm 13\%$ for reactors A and B (without bad period), respectively.
- Scaling is observed in the cathode chamber on both the electrodes and the membrane surface resulting in increasing cell potentials. Periodic cleaning with hydrochloric acid can be used successfully to remove the scaling.
- The cathode potentials did return to their original value after cleaning of the cathode compartment with a 0.01M hydrochloric acid solution.
- The oxygen concentrations at the end of the rising main are below 1 mg/L .

3.0 Cathodic caustic generation

3.1 Experimental Methodology

3.1.1 Laboratory Set-up & Procedures

The two-chambered electrochemical cell consisted of two parallel Perspex frames separated by a cation exchange membrane (Ultrex CM17000, Membranes International Inc., Glen Rock, NJ, USA). The internal dimensions of the anode and cathode compartment were both $19.5 \times 4.8 \times 0.9 \text{ cm}^3$. This created a volume for the anode and cathode compartment of about 84 mL . Pt/Ir ($\text{PtO}_2/\text{IrO}_2$: 0.70/0.30) coated titanium electrodes (diameter: 240 mm; thickness: 1 mm; specific surface area: $1.7 \text{ cm}^2/\text{cm}^2$) with a projected surface area of 24 cm^2 were used as the anode and cathode material (Magneto Anodes BV, The Netherlands). In all experiments, an Ag/AgCl (RE-



5B, Bio Analytical, USA) was used as the reference electrode (+197 mV versus SHE). Domestic wastewater was fed to the anode chamber at a flow rate of 9.1 L h^{-1} using a peristaltic pump (Watson Marlow, UK). A recirculation flow was kept at 40 L h^{-1} to obtain a good mixing rate in the anode chamber by using a peristaltic pump (Watson Marlow, UK). The domestic wastewater was stored at 4° Celsius . Prior to use, the domestic wastewater was heated up to ambient temperatures using a water bath. A 10 g L^{-1} NaCl solution was used in the cathode chamber. The NaCl solution (125 mL) was constantly recirculated over the cathode chamber using a small peristaltic pump (Midstreams Instruments, Australia).

The experiments were performed in a batch mode and controlled galvanostatically using a Wenking potentiostat/galvanostat (KP07, Bank Elektronik, gmbH, Germany). In every experiment, the cell was operated for 4 hours. Here, in every alternate batch the anode was used as a cathode and vice versa. The anode and the cathode potentials were recorded every minute using an Agilent 34970A data acquisition unit. The current efficiency was calculated as the ratio between the amount of charge transfer used for the formation of caustic soda (based on the one electron reduction of water to hydroxide) and the total charge added to the system.

3.1.2 Analytical Methods

The analytical methods used for the laboratory scale experiments for the determination of the pH and conductivity was previously described in detail in the progress report of August 2009 (TAC progress report August 2009). In addition, the pH was also measured by means of titration. The ammonium concentrations were analysed using a Lachat QuikChem8000 (Milwaukee) flow injection analyser (FIA). Elements (e.g. Sodium, Potassium, and Calcium) were measured by means of inductively coupled plasma optical emission spectrometry using a Perkin Elmer ICP-OES Optima 7300DV instrument (Perkin Elmer, USA).

3.2 Results and discussion

An overview of the results of the efficiency of cathodic caustic generation is detailed in Figure 3.1.

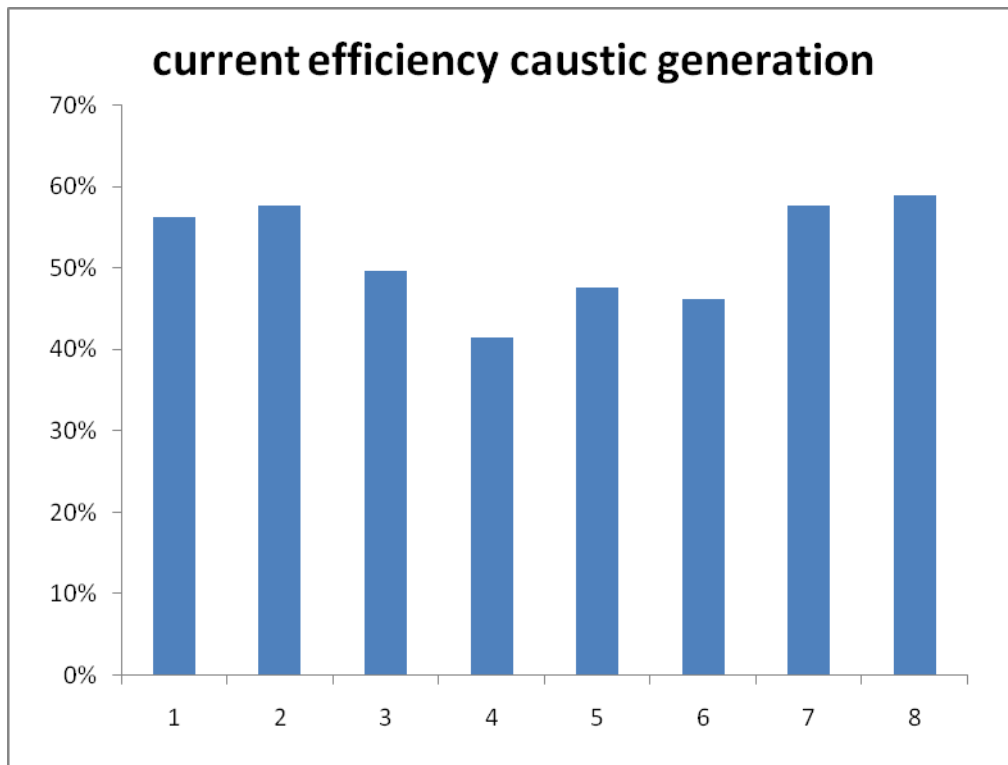


Figure 3.1. Current efficiency of caustic generation from domestic wastewater using Pt/Ir coated titanium electrodes at a current density of 100 A m^{-2} .

- The average current efficiency for the generation of caustic at a current density of 100 A m^{-2} was $52 \pm 7\%$ ($n=8$). This means that cations other than sodium, potassium and calcium were transported through the membrane. Since FIA analysis showed that the transport of ammonium was insignificant, protons must have been transported from the anode to the cathode. The pH of domestic wastewater is normally around 7 and thus contains a low proton concentration (i.e. 10^{-7} M). However, locally at the electrode surface the pH can be very low due to the oxidation reactions occurring on the electrode surface area. If there is not sufficient mixing, a high proton concentration near the membrane is obtained and can thus result in significant crossover of protons.
- Analysis of the cathode water-lock showed that the amount of ammonia stripped as a result of crossover of ammonium from the anode to the cathode was insignificant.

In Figure 3.2 an overview of the anode and cathode potentials during the experiments is presented.

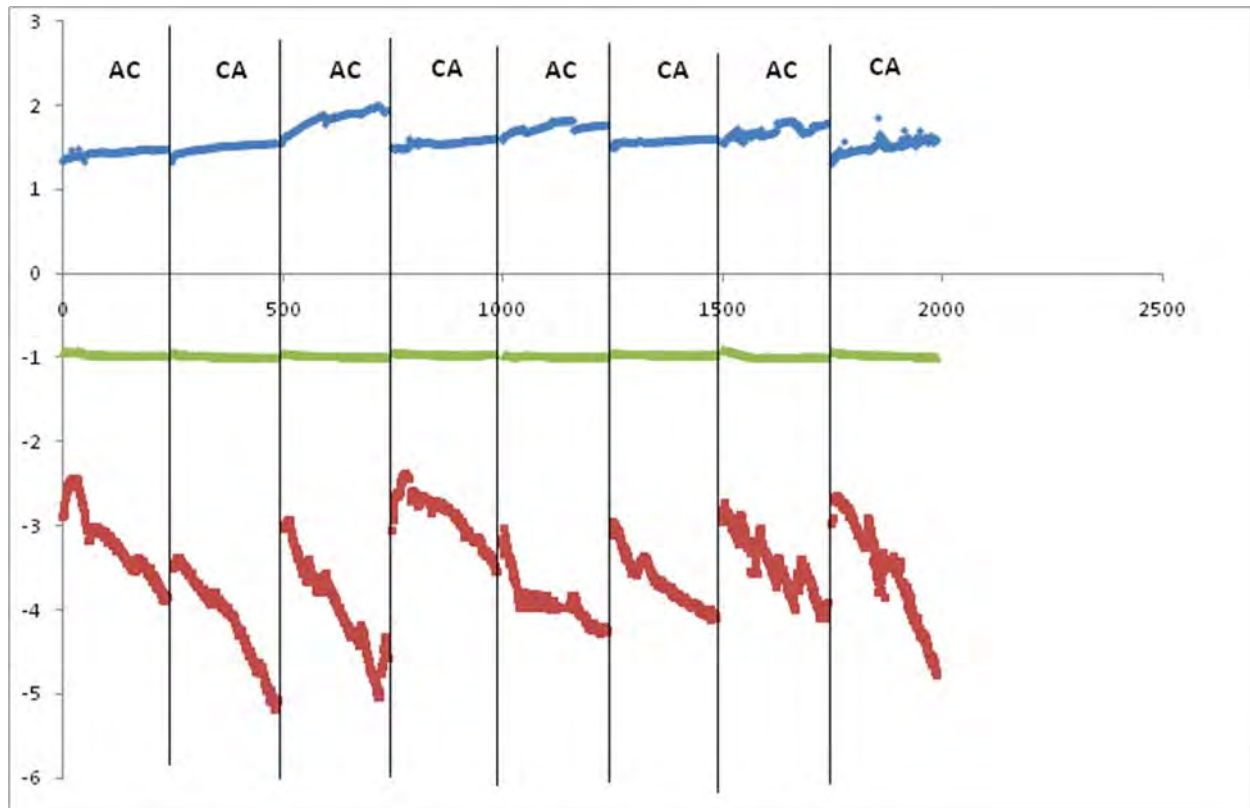


Figure 3.2 Anode (blue), cathode potential (green) and cathode potential+internal resistance (red) during the anodic oxygen generation coupled to cathodic caustic generation from domestic wastewater using Pt/Ir coated titanium electrodes at a current density of 100 A m^{-2} .

- Figure 3.2 shows that the internal resistance of the system increases as a result of scaling in the cathode chamber (visually observed).
- Polarity switching enables a reduction in the internal resistance, where cathode potentials return to their original values (i.e. approximately -3 Volt).



4.0 Discussion

Table 4.1. highlights the progress against milestones for SP7, as valid on February 21st 2011 are presented.

In-situ oxygen generation

The anodic half-cell tests indicated that the obtained indirect sulfide oxidation rate from domestic wastewater is independent of the anode material used. Furthermore, it was shown that oxygen can be generated in-situ at a current density of 100 A m^{-2} at a cell potential of approximately 5 V (i.e. the target current density and cell potential as described in the research proposal). This was also demonstrated during the field trials. Applying a higher current density would result in a decrease in investment costs (i.e. less electrode material is needed). However, it would result in an increase in operational costs since higher cell voltages are expected. Furthermore, initial experiments to determine the efficiency of in-situ generation of dissolved oxygen showed a decrease in dissolved oxygen efficiency at increasing current densities. Hence, the outcome of the experiments to verify the efficiency of the dissolved oxygen concentration in combination with the observed cell potentials will determine the optimum current density.

Table 4.1. Overview of milestones for SP7 and their status

	Milestone	Date	Percentage complete	Remarks
1	Anode materials for sulfide oxidization selected	July 2009	100%	Five different electrodes with different catalytic activities have been tested. All materials are suitable for in-situ oxygen generation. BDD will not be tested.
2	Cathodic process and cathode material selected	December 2009	95%	Principle demonstrated. Further development of H_2O_2 formation on a cathode is now beyond the scope of SP7, but will feed in again later from other projects at the AWMC. Principle of cathodic caustic soda generation demonstrated, and further development is in progress.
3	Optimal operational conditions determined (critical)	December 2009	95%	Efficient oxygen generation demonstrated. Further input will follow from on site tests if sulfide removal to low concentrations (i.e. $<1 \text{ mg L}^{-1}$) can be achieved by a sole anodic process. Principle demonstrated during field trials. Further development of polarity switching to overcome scaling and determine efficiency of dissolved oxygen concentrations in progress.
4	Working principle demonstrated on synthetic wastewater	March 2010	100%	
5	Working principle	March 2010	95%	Working principle demonstrated in the



	Milestone	Date	Percentage complete	Remarks
	demonstrated on real wastewater (critical)			laboratory. Principle demonstrated, further development of polarity switching to overcome scaling in progress.
6	Reactor design with respect to main engineering considerations determined (critical)	<i>February 2010</i>	100%	A meeting was held in the TAC meeting of 26 th August 2010 were the most important engineering considerations were discussed with the industrial partners.
7	Pilot plant design completed and the components ordered	<i>March 2010</i>	100%	On site experiments are currently in operation.
8	Pilot plant operational (critical)	<i>October 2010</i>	80%	On site experiments are currently in operation and will be finalized the coming period.
	Optimal operational conditions for pilot plant defined	<i>October 2011</i>	50%	In progress.



5.0 IMPLICATIONS FOR INDUSTRY

The results of the on-site experiments show that sulfide can be removed to concentrations below 1 mg L^{-1} from domestic wastewater under realistic sewer conditions using Ta/Ir coated titanium electrodes. Based on an average cell potential of 5 Volt, a price of $\$0.06/\text{kWh}$ and an oxygen generation efficiency of 95 %, the cost per kg of oxygen is $\$1.06 \text{ kg}^{-1}$, relative to $\$0.74 \text{ kg}^{-1}$ for standard oxygen purchases. However, the efficiency of dosing is expected to be higher due to fine dispersion of oxygen. Currently, experiments are underway to determine the current efficiency for in-situ oxygen generation, based on the generation of dissolved oxygen.

An increase in cell potential (i.e. from 4.5 V to approximately 12 V) as result of scaling in the cathode chamber was observed, requiring the need for periodic cleaning of the cathode chamber with an acid solution or by polarity switching. Switching the polarity is preferable from an operational point of view as it only requires a change in the direction of the flow (i.e. anode becomes cathode and vice versa). Hence, the handling, transport and storage of chemicals (hydrochloric or citric acid) may be avoided. The feasibility of polarity switching as a means to overcome scaling issues is currently being investigated using Pt/Ir electrodes. However, regular switching of the polarity is expected to have a negative impact on the lifetime of the electrodes. Therefore, it is important to accurately assess the required frequency of polarity switching. Accelerated lifetime test are required to determine the expected lifetime of the electrodes under the operational conditions applied. These experiments have already been planned for the upcoming period in collaboration with our supplier.

For the successful application of an electrochemical system in sewers at full scale, 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, 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, where hair and rags tend to cling onto. The design of the electrochemical cell must be as such that large obstacles can flow freely through the sewer pipe and electrochemical reactor. In general, blockage of the electrochemical cell may be avoided if the dimensions of the anode compartment are at least equal to those of the electrochemical cell. Valves are needed to switch the flow in the electrochemical cell for polarity switching (i.e. the anode compartment becomes the cathode compartment and cathode compartment becomes the anode compartment). Prevention of particle and biomass accumulation can be avoided by applying a sufficient up-flow velocity. In general, an upflow velocity of 0.6 m s^{-1} used in the rising main is sufficient to avoid any particle and biomass settling. Large temporal as well as spatial variations in the wastewater composition (i.e. sulfide, organics and sulfate concentrations) can be observed in the sewer systems. In this study, significant fluctuations in sulfide influent concentrations, ranging between 3.77 to 10.68 mg L^{-1} were observed. Hence, these fluctuations can have a significant impact on the energy requirement. The placement of an online sulfide sensor, such as a catscan sensor which has been successfully applied, downstream of the electrochemical cell will allow further fine tuning of the system. Wastewater flows through sewer networks vary significantly over time, resulting in large fluctuations in hydraulic retention times (HRT). Furthermore, in rising mains, the pumps are often turned on and off causing intermittent flow. Thus, in order to successfully apply this novel technique, the placement of the electrochemical cell in the sewer system is critical. The implementation of a working dynamic model (as developed by the AWMC) should be used to accurately assess the location at which the electrochemical cell should be implemented.



Anodic oxygen generation can be coupled with cathodic caustic generation. At the moment we are capable of generating caustic soda (coupled with in-situ oxygen generation) at an efficiency of $52\pm 7\%$ at a current efficiency of 100 A m^{-2} . Regular switching between the anode and cathode configuration was successful to overcome scaling issues. Preliminary results indicate that the efficiency of caustic generation is directly influenced by the distance between the electrode surface and the cation exchange membrane (data not shown). Currently, experiments are underway with an optimized setup (optimized flow regime for optimal mixing) to determine the impact of the mixing on the transport of protons through the cation exchange membrane (and thus the efficiency of cathodic caustic generation).