SP7: ELECTROCHEMICAL ABATEMENT OF SULFIDE IN SEWER SYSTEMS

BACKGROUND

In view of the practical limitations of existing strategies for sulfide control in sewers, there is a general interest for new sulfide abatement technologies. In the perspective, electrochemical methods may be of interest. In an electrochemical system, an electrode can be poised at a certain potential when present in the liquid stream. Reactive compounds such as sulfide can be oxidized by such an electrode (anode). The anode is linked to a counter electrode; the cathode that reduces spatially separated electron acceptors, such as oxygen. The redox control by an electrode will affect the redox potential in the surrounding aqueous matrix. It has already been shown that sulfide can be oxidized to elemental sulfur at anodes. Elemental sulfur is an interesting end product, as depending on the pH it will precipitate in small granules. Only at pH values higher than 7, the sulfur can again dissolve as polysulfides. An electrode could be submerged continuously in the wastewater, and thus continuously control the redox potential so sulfide is oxidized. During an electrochemical process, no organic substrate would be removed, as sulfide is substantially more reactive.

Recent advances in electrode development and operation have enabled an increased interest in electrochemical sulfide abatement strategies. As the main rationale, electrochemical abatement comes with:

1. A high degree of controllability, hence better fine-tuning of dosing (of electricity in this case)
2. Less to almost no carbon loss due to the selectivity of the oxidation process, thus preserving the carbon sources for the down-stream biological nutrient removal
3. Low in peripherals, no storage required of chemicals nor transport
4. Inherently safe as no explosive gases or reactive chemicals are used in significant quantities at any time point
5. Supply of electricity is generally straightforward, as it has a high availability
6. Potentially significantly cheaper

The main disadvantages of the electrochemical strategies are:

1. They have not yet been tested in sewer systems (they exist for wastewater treatment such as textile and slaughterhouse wastewaters).
2. Sulfur particles, which are generated and released in the flow, end up in the biosolids at the WWTP and are potentially reduced there. Whether this affects the current odour issues these biosolids pose is as yet to be assessed.

Currently, if oxygen is used as oxidant for sulfide, it is injected in pure form or as air in the sewer system. With the electrochemical method, it is aimed to produce oxygen in situ through electrochemical production of oxygen. The advantages of in situ generation in comparison to traditional methods for oxygen supply are: fine dispersion, high transfer efficiency, rapid controllability, easy to monitor.

The electrons generated at the anode need to be discharged at the cathode. The possibility of producing hydrogen peroxide at the cathode using the electron received from sulfide oxidation could also be an interesting outcome. If successful, hydrogen peroxide produced could be added to the downstream sewer for continued sulfide control.

There are currently two methods known for the electrochemical generation of hydrogen peroxide:

- Oxidation of water at low pH at an anode
- Reduction of oxygen at high pH at a cathode

In this project, it was aimed to achieve the latter, as a strong pH increase at the cathode is expected due to imperfect proton diffusion from the anode. If the current densities of around 1200 A m^{-2} could be achieved, it appears unlikely that the cathodic conversion rate would be limiting.

OBJECTIVES

SP7 has the following objectives:

- To determine the electrode materials and operational strategies to electrochemically oxidize sulfide in sewer systems
- To test the proposed concept on pilot scale at a trial site
- To investigate the overall effect of the electrochemical abatement on the downstream sulfide related issues and on the conservation of organics
- To assess the economical and practical potential of electrochemical sulfide removal in sewer systems

POTENTIAL BENEFITS

The followings outcomes and benefits are expected from the sub-project.

1. A method for the oxidation of sulfide by electrochemical means in sewer systems, either
    - Directly by oxidation of sulfide to elemental sulfur at the anode
    - Indirectly by in situ oxygen generation which reacts in solution with sulfide
2. A cathodic process to allow discharge of the electrons gained from the sewer. In one embodiment the product of the cathodic reduction will be hydrogen peroxide, which can be added to sewers for downstream sulfide control
3. Field based knowledge on the operation of electrochemical sulfide removal systems
4. A proof of concept for cost effective, flexible sulfide removal, suitable for further development and implementation in the Australian sewer network

METHODS AND APPROACHES

This study employs the following methods and approaches.

LABORATORY STUDY – SELECTION OF ELECTRODES

Small electrochemical cells were set up, each consisting of an anodic and a cathodic compartment, separated by a cation exchange membrane. For anodic tests, a stainless steel counter cathode was used, which produced hydrogen in situ. For cathodic tests, the oxygen anodes were left in place. A number of anode materials were tested for the following specific purposes.

- Anodic sulfur oxidation
- Anodic oxygen generation
- Standard cathodic process
- Cathodic hydrogen peroxide generation

Preferred anode materials were selected based upon the results of the above studies. In addition, kinetic data for the design of complete electrochemical cell will also be collected.

LABORATORY STUDY- BATCH CELL TESTING

The electrodes selected above were used in batch cell configuration using synthetic sulfide medium. Both the direct sulfide oxidation and the oxygen generation were tested. The batch cell consisted of a simple electrochemical block cell equipped with the chosen anode and cathode of separated by a membrane.

The batch cell was recycled over a buffer vessel containing the synthetic sulfide medium and connected to a potentiostat/galvanostat. The system was controlled on either current generation or anode potential. The sulfide concentration was monitored with online sulfide sensors and offline chemical analysis to assess the performance of the system. Furthermore, the anodes were monitored with respect to their susceptibility to sulfur deposition, which could lead to deactivation of the electrode.

After the batch cell testing on synthetic sulfide medium, the direct oxidation and the oxygen generation method was tested with real wastewater. This was done in the same batch cell. Besides sulfide, the real wastewater contains a broad variety of organic compounds. To monitor undesired COD loss associated with the treatment method, total soluble COD was monitored in parallel to the sulfide removal.

Operational parameters for direct oxidation of sulfide and indirect oxidation of sulfide using oxygen were established. Also, the effects of organics in the real wastewater on both processes and vice versa were evaluated.

PILOT PLANT TESTING

A pilot plant configuration was developed and tested. The design needed to be robust and unsusceptible to clogging. The best combination of anode and cathode from laboratory batch cell testing was used in the design. The pilot plant was tested onsite under real wastewater conditions. Design and operational characteristics for an electrochemical system for sulfide removal in sewer systems were established.

OUTCOMES

BETTER UNDERSTANDING OF THE PROCESS

- Five different electrodes with different catalytic activities have been tested. All materials are suitable for in-situ oxygen generation.
- The anodic half-cell tests indicate that the obtained indirect sulfide oxidation rate from domestic wastewater is independent of the anode material used.
- Principle of cathodic caustic soda generation has been demonstrated.
- With in-situ oxygen generation being the main aim higher current densities can be achieved, as the mass transfer of sulfide towards the electrode does not need to be taken into account.
- 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.
- Methods for controlling inorganics scaling on electrode surface have been developed.
- The experimental results showed that caustic generation is the most cost-effective electrochemical approach.

ESTABLISHMENT OF OPERATING CONDITIONS/PARAMETERS

- Efficient oxygen generation under the operating conditions employed has been demonstrated. On site tests have revealed that sulfide removal to low concentrations (i.e.<1 mg L^{-1}) could be achieved by a sole anodic process.
- Caustic can be produced from domestic wastewater 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 successful to overcome problems of scaling.
- The use of spacers did not increase the caustic recovery, but higher cell voltages were obtained.

DESIGN OF A PILOT PLANT AND DETERMINATION OF OPTIMAL OPERATING CONDITIONS

Based upon the findings of the laboratory experiments, a pilot plant to demonstrate the application of an electrochemical system in a full-scale sewer was designed. Several process and engineering issues were considered in the design.

- Prevention of ragging, blockage of the electrochemical system and the use of valves - 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. 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
- Prevention of particle and biomass settling and accumulation, precipitation of inorganics by using high upflow velocity
- Consideration of diurnal flow variations
- Methods for minimizing electrode losses

DEMONSTRATION OF COST EFFECTIVENESS AND PRACTICAL POTENTIAL OF AN ELECTROCHEMICAL SYSTEM

Experimental results in this study have shown that caustic generation is the most cost-effective electrochemical approach. Based on the current efficiency obtained and cell voltage applied, cost calculations have shown that the costs for sulfide abatement can be reduced from AUS \$2.5-9.4 kg S^{-1} (for conventional chemical dosing) to AUS \$0.83-1.17 kg S^{-1}. Thus, the economic potential of electrochemical caustic generation from sewage as a solution to sewer corrosion and odour problems is demonstrated. In addition to this, practical potential of the technology has been illustrated through the pilot plant trial in Gold Coast.