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A Comparative Study of Sulphite Oxidation Under Alkaline Conditions by Use of Wall-jet Flow Cell and Rotating Disc Electrode

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The oxidation of sulphite under alkaline conditions has been studied in a diffusion-controlled region in order to find the relationship between the limiting current and the concentration of sulphite in a solution. Cyclic voltammetric experiments with a rotating disc electrode were used to define the potential region where the oxidation current was diffusion controlled. Chronoamperometric experiments with a "wall-jet" flow cell gave a linear relationship between the limiting oxidation current and $(C_{SO_3^{2-}})^{3/2}$. This electrochemical method can therefore be used to monitor changes in the sulphite concentration in real time.

Keywords*:* Wall-jet flow cell; Sulphite; Alkaline; Analytic method.

List of symbols

C^{∞} [mol L^{-1}]	Bulk concentration
D [$m^2 s^{-1}$]	Diffusion coefficient
F [96487 A s mol^{-1}]	Faraday's constant
i_L [A m^{-2}]	Limiting current density
n	Number of electrons
t [s]	Time
ω [rpm]	Rotation rate
δ [m]	Thickness of diffusion layer

1. INTRODUCTION

Corrosion is an important factor that must be taken into account in the design and maintenance of a district heating system. The corrosion rate inside steel pipes is normally related to the hydrogen ion concentration and the oxygen content in the water. Therefore, in order to lower the corrosion rate, hydroxide is added to the water to raise the pH to around 9.5. Oxygen is usually removed by heating the water [1,2].

Dithionite and sulphite are also commonly used as oxygen scavengers. They react with dissolved oxygen to form sulphate (SO_4^{2-}). These compounds are added to fresh water in closed district heating systems in order to remove remaining oxygen from raw feed water. However, an excess of any of these components may decompose to sulphides, which also contribute to an increase in the corrosion rate.

In some district heating systems geothermal water is used as the heating source. Geothermal water often contains sulphur components like sulphide, dithionite and sulphite that are released into the water from the ground itself. The presence of sulphide may also come from sulphate reducing bacteria (SRB) activity under e.g. deposits. If the SRB have access to sulphate they will produce sulphide.

The sulphur compounds in general are very reactive and may exist in many oxidation states. Often several oxidation states of sulphur coexist in a solution. The range of oxidation states for sulphur is shown in Table 1. An overview of sulphur reactions is given elsewhere [3,4].

Table 1. Oxidation states of sulphur.

6	6	5	4	3	5/2	2	2	0	-2/5	-1/4	-1	-2
$S_2O_8^{2-}$	SO_4^{2-}	$S_2O_6^{2-}$	SO_3^{2-}	$S_2O_4^{2-}$	$S_4O_6^{2-}$	$S_5O_6^{2-}$	$S_2O_3^{2-}$	S	S_5^{2-}	S_4^{2-}	S_2^{2-}	S^{2-}

An excess of sulphur components like sulphide, dithionite and sulphite in the water may lead to the formation of an iron sulphide film on the steel surface, which can affect the corrosion rate of the steel. The corrosion properties of iron sulphide at low pH are known from the oil industry and studies have been published in several papers [5-10]. The number of studies performed in alkaline solutions is more limited [11-16].

The scope of the work presented in this paper has therefore been to obtain real time information on the concentration of the different sulphur components in alkaline fresh water by using an electrochemical method. Chronoamperometry was used to study the reactions of SO_3^{2-} (sulphite) in alkaline fresh water solutions. This method gives the oxidation current at a fixed potential within the potential range where the oxidation reaction is entirely diffusion controlled. If the flow rate is kept constant, the limiting current is a function of the bulk concentration of the electro-active species. A rotating disc electrode is often used for electro-analytical purposes, but since this setup requires mechanical movement of the electrode it is not very useful in an industrial environment [17]. The experiments were therefore performed by use of a "wall-jet" flow cell, which is easier to apply in an industrial environment.

2. EXPERIMENTAL

2.1. Methods

Cyclic voltammetric (CV) measurements were performed using a rotating disc electrode. The set up is shown in Fig. 1. A three-electrode cell configuration was used consisting of a rotating platinum disc working electrode ($A = 0.20\ cm^2$), a stationary platinum counter electrode ($A = 0.48\ cm^2$) and a saturated calomel reference electrode. The electrodes were controlled using a bipotentiostat

(Ecochemie), which was connected to a Hewlett Packard Pentium II PC with Windows 95 and PGSTAT 10 software. A modulated speed rotator from Pine Instrument Company rotated the working electrode. To obtain a fresh cross section surface of the working electrode it was polished for 5 minutes with SiC-emery paper, 4000 grit (Struers). The electrode was washed in distilled deionised water in order to remove adsorbed SiC particles from the surface. The potential sweep rate was 20 mV per second for all CV experiments starting at a potential of -0.85 V versus a saturated calomel electrode (SCE, + 0.241 V vs SHE).

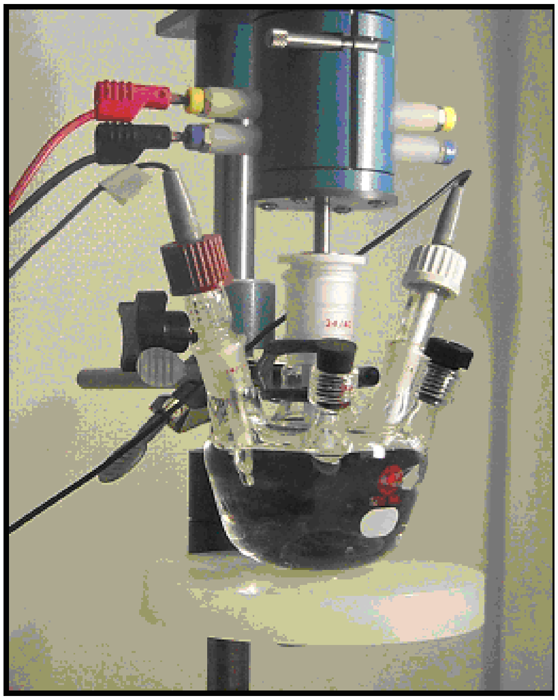

Figure 1. Cell with rotating disk electrode equipment.

Chronoamperometry experiments in this study were performed using the cell configuration shown in Fig. 1 and a wall-jet flow cell. The set up of the wall-jet flow cell is based on work of Gasana et al. [16] and is shown in Fig. 2. The cell has a three-electrode configuration with a high purity platinum disc working electrode, a graphite rod counter electrode and a saturated calomel reference electrode. An in-house fabricated working electrode was used. A platinum rod (3.0 cm length, 0.3 cm diameter) was positioned on a copper base to ensure electrical contact and covered with epoxy resin (Epofix kit, Struers) to give an exposed area of 0.071 cm^2. A fresh electrode surface was obtained by polishing it with Buhler SiC-emery paper, type 1200, for 30 seconds. The surface was further polished on a Struers Planopol-2 polishing machine using a polishing cloth with Buhler aluminium oxide powder of 1 and 0.05 μm particle size fineness for 5 and 10 minutes, respectively. The electrode was cleaned in an ultrasonic bath for 5 minutes in distilled water and for 5 minutes in ethanol.

The flow was directed onto the working electrode through a nozzle, positioned a few millimetres from the electrode. The flow rate was adjusted by a reduction valve and monitored on a flow meter. A peristaltic pump was used to circulate the electrolyte from the reservoir through the cell. The

$[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox system was used to optimise the different parameters such as the flow rate and the distance between the nozzle and the electrode [16].

The potential was raised from the open circuit potential, E_{OCP}, where no reactions occur to a potential, E_2, (within the potential range 0.95 – 1.20 V SCE) where the oxidation reaction rate is diffusion controlled.

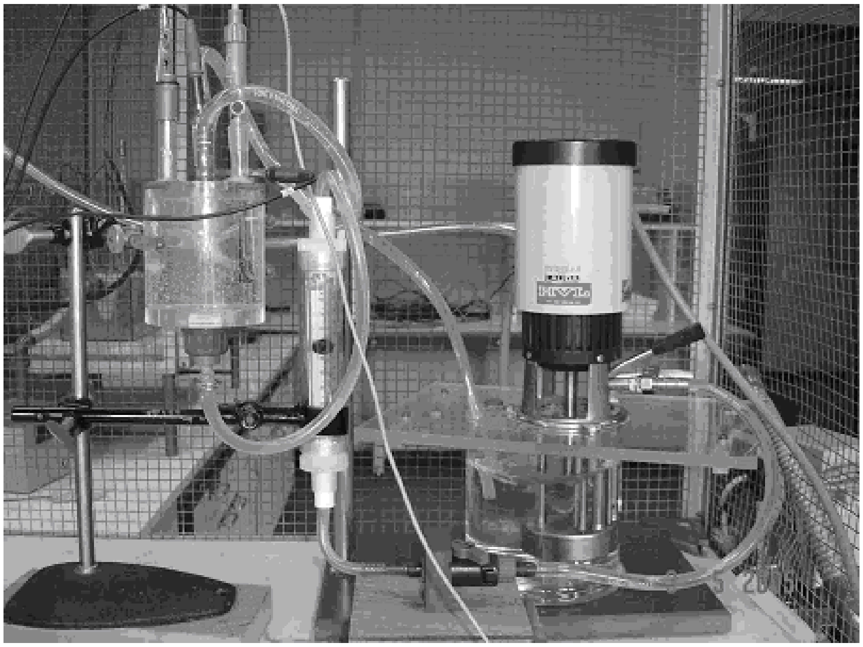

Figure 2. Wall-jet flow cell with pump unit.

2.2. Reagents

The water used in the experiment was purified through an ion exchange resin, and had a conductivity of 1.70 μS/cm. The chemicals used were Merck 98 % sodium sulphite and Riedel-de Haën sodium hydroxide of pro analysis qualities. Prior to each experiment a fresh 0.5 M solution sulphite was prepared using oxygen free deionised water. Oxygen was removed from the water by purging it with 99.999 % nitrogen gas for 30 minutes. The stock solution was stored in airtight containers equipped with septum. A syringe was used to transfer the solution from the container to the electrolyte.

To obtain anaerobic conditions in the test electrolytes they were purged with nitrogen gas for at least 30 minutes prior to the addition of chemicals, and a nitrogen atmosphere was kept above the electrolyte as an inert layer during the electrochemical measurements.

0.5 M sodium hydroxide was used in order to obtain the appropriate pH values. The pH of the electrolyte was monitored through the experiment by the use of a pH electrode.

3. RESULTS AND DISCUSSION

Cyclic voltammetric measurements on a platinum rotating disc electrode were done for an alkaline electrolyte of sulphite in order to identify the oxidation potentials for this compound. The polarisation measurements were carried out from -0.85 V to 1.20 V SCE. The low vertex potential is within the potential area for the hydrogen evolution reaction and the high vertex potential is within the potential area for the oxygen evolution reaction. Earlier studies have shown that when the potential of a platinum electrode is cycled between these two potential areas, the electrode surface will consist of an oxide and/or hydroxide layer that is stable and reproducible [17, 18]. Cyclic voltammograms of a 10 mM sodium sulphite solution at different rotation rates of the disk electrode are shown in Fig. 3.

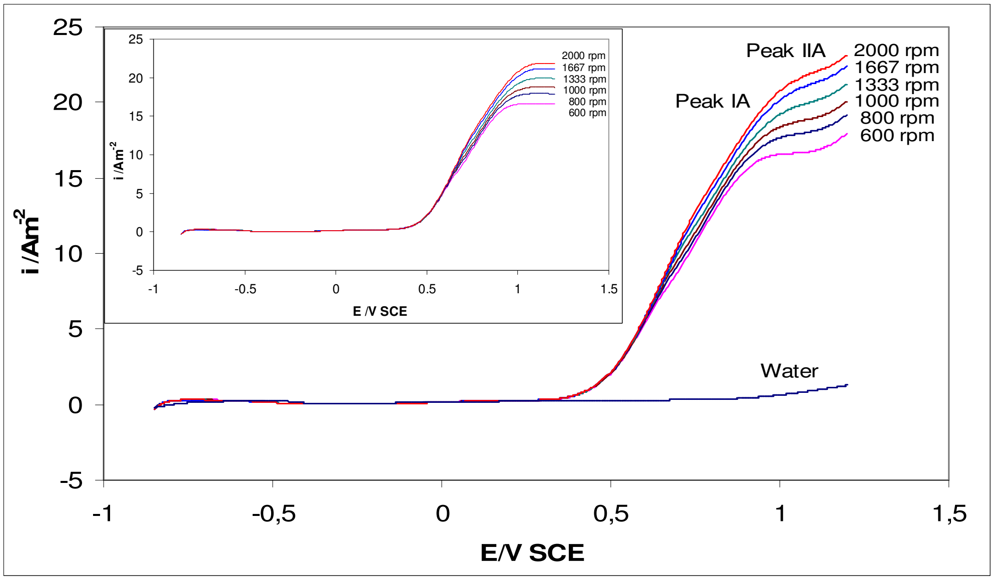

Figure 3. Cyclic voltammograms of a 10 mM sodium sulphite solution on a RDE (600-2000 rpm) with a scan rate of 40 mV/sec and for water (1000 rpm) with a scan rate of 20 mV/sec. In the insert the current contribution from the water oxidation has been subtracted. All experiments are performed at pH 11.

The rotation rate is varied from 600 to 2000 rpm. The oxidation reaction starts at a potential of approximately 0.38 V and the current reaches a plateau at approximately 1.0 V (The peak current plateau is referred to as peak IA in Fig. 3). At potentials higher than 1.05 V the current again increases, referred to as peak IIA in Fig 3. The current of peak IIA is independent of the rotation rate of the electrode and is probably due to the oxygen evolution reaction from water. A voltammogram of the oxidation of water at pH 11 has been included in Fig. 3. The current contribution from the oxygen evolution has been subtracted from the voltammograms in the insert in Fig. 3.

At approximately 0.62 V there is a change in the slope of the voltammograms, which indicates a change in the reaction mechanism. It is previously reported that the oxidation of sulphite on a stationary platinum electrode had two oxidation peaks [19]. When the electrode was rotated, the current peak at high potentials became more pronounced than on a stationary electrode. However, the two peaks could be separated by a change in the slope of the voltammograms as shown in Fig. 3. Analysis of the experimental data showed that sulphite was oxidised through a single electron transfer reaction to a sulphite radical and the two current peaks were found to be an effect of strong adsorption of the oxidation product on the electrode surface [19]. At potentials below 0.62 V the sulphite radical is strongly adsorbed to the electrode. The reaction mechanism is shown in Eqs. (1) - (5).

$$SO_3^{2-}\ (aq) = SO_3^{2-}\ (ad) \tag{1}$$

$$SO_3^{2-}\ (ad) \rightarrow SO_3^{\bullet -}\ (ad) + e^- \tag{2}$$

$$2\ SO_3^{\bullet -}\ (ad) \rightarrow S_2O_6^{2-}\ (ad) \tag{3}$$

$$S_2O_6^{2-}\ (ad) + 2\ OH^- \rightarrow SO_3^{2-}\ (ad) + SO_4^{2-}\ (ad) + H_2O \tag{4}$$

$$SO_4^{2-}\ (ad) = SO_4^{2-}\ (aq) \tag{5}$$

The current contribution from this reaction mechanism will be constant if the rate of the electron transfer reaction, Eq. (2), is faster than the rate of the chemical reaction, Eq. (4).

At potentials above 0.62 V the product of the oxidation reaction was only weakly adsorbed to the electrode. The reaction mechanism is analogue to the one described above.

According to the Levich equation, shown in Eq. (6), there should be a linear relationship between the current and the square root of the electrode rotation rate if the oxidation reaction rate is diffusion controlled [19]. This relationship can be used to analyse the current plateaus in Fig. 3.

$$i_L = 0.62nFD^{2/3}\nu^{-1/6}c^{\infty}\omega^{1/2} \tag{6}$$

Fig. 4 shows the current of the peak plateau in Fig. 3 as a function of the square root of the rotation rate of the electrode.

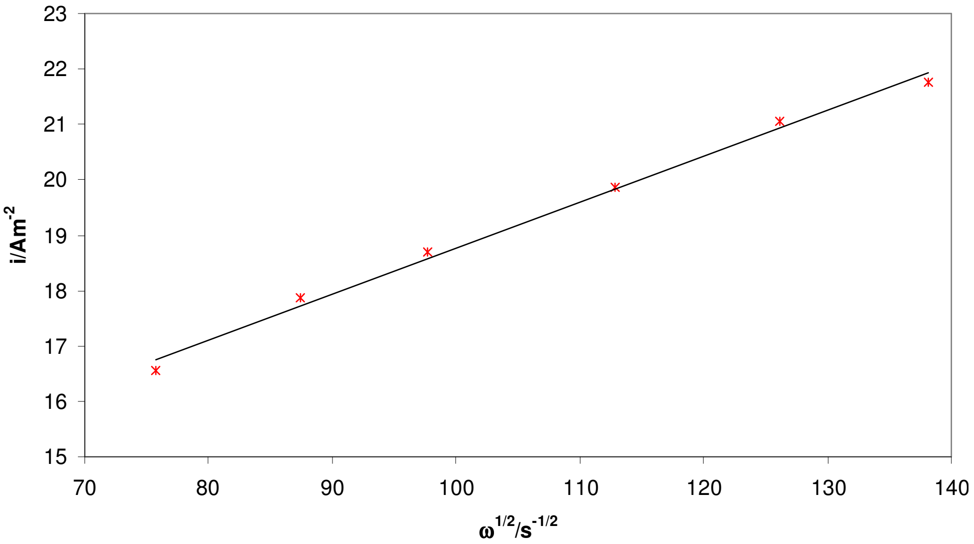

Figure 4. Limiting current density plotted versus the square root of the rotation rate of the electrode. The electrode potential is 1.13 V.

There is a good linear relationship between the current and the square root of the rotation rate, which implies that it should be possible to use this relationship to obtain information about the concentration of sulphite in a solution. However, when the plot in Fig. 4 is extrapolated to zero rotation rate, the current is approximately 10 A/m^2. The deviation from the Levich equation is probably caused by a constant current contribution from the oxidation reaction that involves a strongly adsorbed reaction product as shown in Eq. (2). At potentials where the electron transfer reaction rate is faster than the reaction rate of the following chemical reaction the product of the oxidation reaction will saturate the electrode surface and the current will become a function of the rate of product removal from the electrode surface by the following chemical reaction. The current contribution from this oxidation reaction will therefore be independent of the rotation rate of the electrode.

Chronoamperometric experiments with a stationary electrode will also show if the reaction is diffusion controlled. The Cottrell equation, shown in Eq. (7), predicts that the current density multiplied by the square root of the time, ($i \cdot t^{1/2}$), plotted as a function of time should be constant for a given concentration if the reaction is diffusion controlled [20].

$$it^{1/2} = \frac{nFD^{1/2}c^{\infty}_{(SO_3^{2-})}}{\pi^{1/2}} \qquad (7)$$

However, as shown in Fig. 5, the relationship between ($i \cdot t^{1/2}$) and time is not constant.

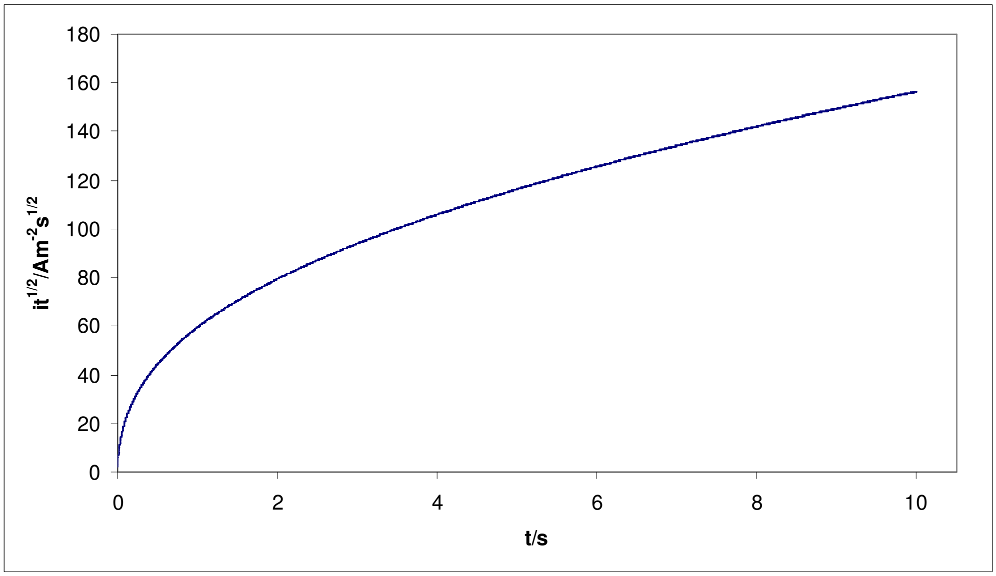

Figure 5. $i \cdot t^{1/2}$ as a function of time for the oxidation of 20 mM sulphite solution on a stationary platinum electrode at 1.05 V, pH 11.

The deviation from Cottrell's equation indicates that the oxidation reaction is not purely diffusion controlled but also affected by kinetics. This result is consistent with the results from the CV experiments.

The flow in a wall-jet flow cell can be compared with the flow regime of a rotating disc electrode. Chronoamperometric data were obtained during 60 minutes using a wall-jet flow cell set-up. The flow rate and pH of the solution was kept constant. The concentration of sulphite was increased from 10 to 30 mM between each experiment.

The potential was changed from the open circuit potential, E_{OCP} to E_2=1.0 V. At a potential of 1.0 V the current is a linear function of the square root of the rotation rate of the electrode in CV experiments, as shown in Fig. 3. Current curves as a function of time at different concentrations are shown in Fig. 6.

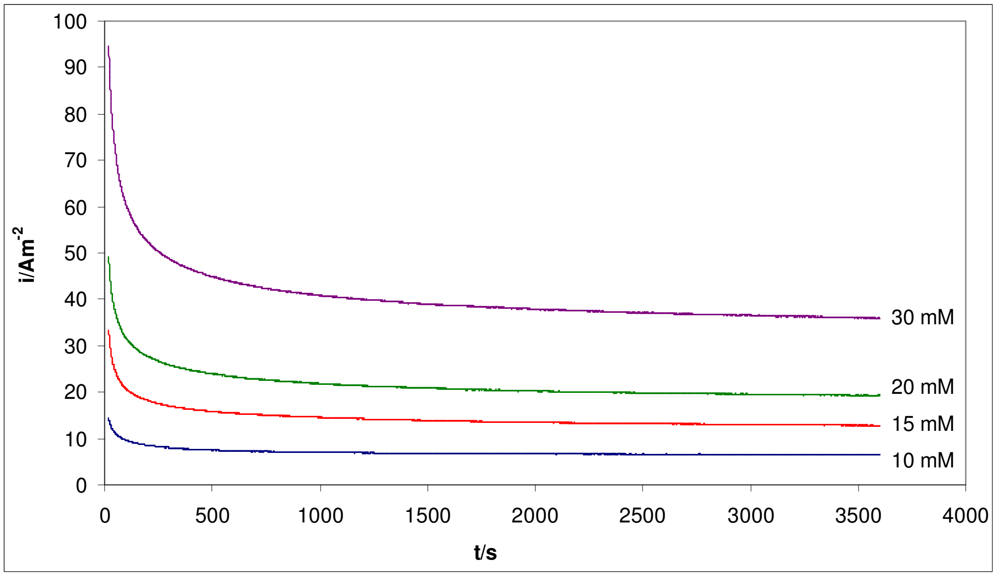

Figure 6. Current density plotted versus time for different concentrations of sulphite, at a constant potential of 1.0 V SCE. The data are taken from a wall-jet flow cell with a constant flow rate of 1.2 L/min. The pH is 11.

Values of the steady state current densities, i, for the different sulphite concentrations are obtained after 3600 seconds in Fig. 6 when the diffusion gradients in the Nernst diffusion layer are constant. The current values are given in Table 2.

Table 2. Limiting current values obtained after 3600 seconds in Fig.6.

Bulk concentration [mM]	10	15	20	30
i [A/m^2]	6.55	12.84	19.30	35.99

Since the flow in the wall-jet flow cell is comparable to the flow regime of a rotating disc electrode, Eq. (6) should still apply to a simple electron transfer reaction if the reaction rate is controlled by the diffusion of reactant to the electrode. When the flow rate is kept constant the limiting current should be a linear function of the bulk concentration of the reactant. But, as can be seen from the proposed reaction mechanism, Eqs (1) – (5), the sulphite oxidation reaction is not a simple electron transfer reaction. The sulphite oxidises to an unstable sulphite radical that undergoes a chemical reaction and forms dithionate. Dithionate will decompose further to sulphite and sulphate. The amount of sulphite available for oxidation under diffusion control may therefore be higher than predicted by the diffusion of sulphite to the electrode surface. The added amount of sulphite will depend on the decomposition rate of dithionate, and if the decomposition reaction takes place on the electrode surface or in the solution. This gives two borderline cases for the relationship between the current and the sulphite concentration.

Case 1 is obtained if dithionate is transported away from the electrode before it decomposes into sulphite and sulphate. The reaction should behave like a normal diffusion controlled reaction and the current should be a linear function of the bulk concentration of sulphite. Fig. 7 show the current obtained after 3600 seconds in Fig. 6, as a function of the bulk concentration of sulphite.

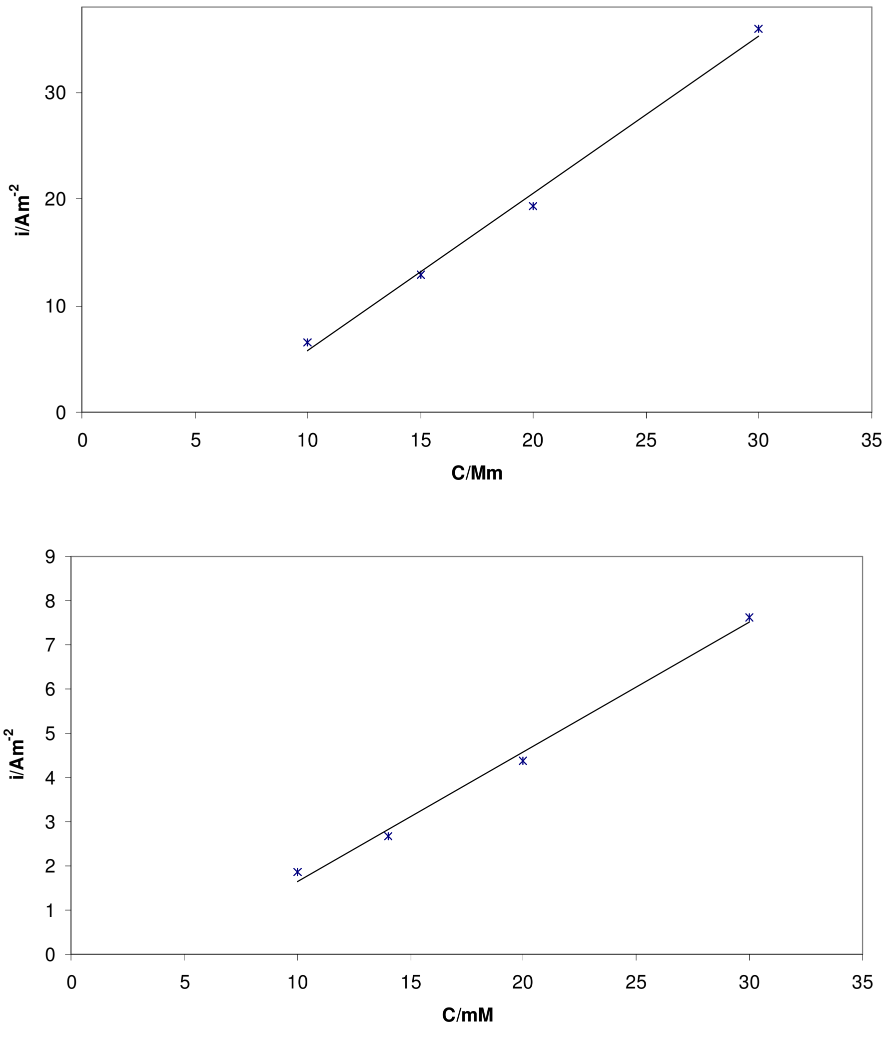

Figure 7. Chronoamperometric current data (E_{OCP} to E_2=1.0 V) versus the bulk concentration of sulphite at pH 11 obtained a) after 60 minutes by wall jet with flow rate 1.2 L/min and b) after 90 minutes by rotating disc electrode at 600 rpm.

As can be seen from Fig. 7a there is a good linear relationship between the current density and concentration. However, when a linear regression line is fitted to the data it does not pass through origin at zero current. The intercept with the concentration axis gives a sulphite concentration of approximately 6 mM. This result indicates that at least some of the sulphite is regenerated at the electrode surface. As shown in Fig 7b a similar result was obtained in a chronoamperometric experiment with a rotating disc electrode set up.

Case 2 is obtained if dithionate is completely transformed to sulphite and sulphate and the decomposition reaction is limited to the electrode surface. For every mole of sulphite that is oxidised half a mole will be regenerated from the decomposition reaction. The current will therefore be a function of $(C_{SO_3^{2-}})^{3/2}$. The current, obtained after 3600 seconds in Fig. 6, as a function of $(C_{SO_3^{2-}})^{3/2}$ is shown in Fig. 8.

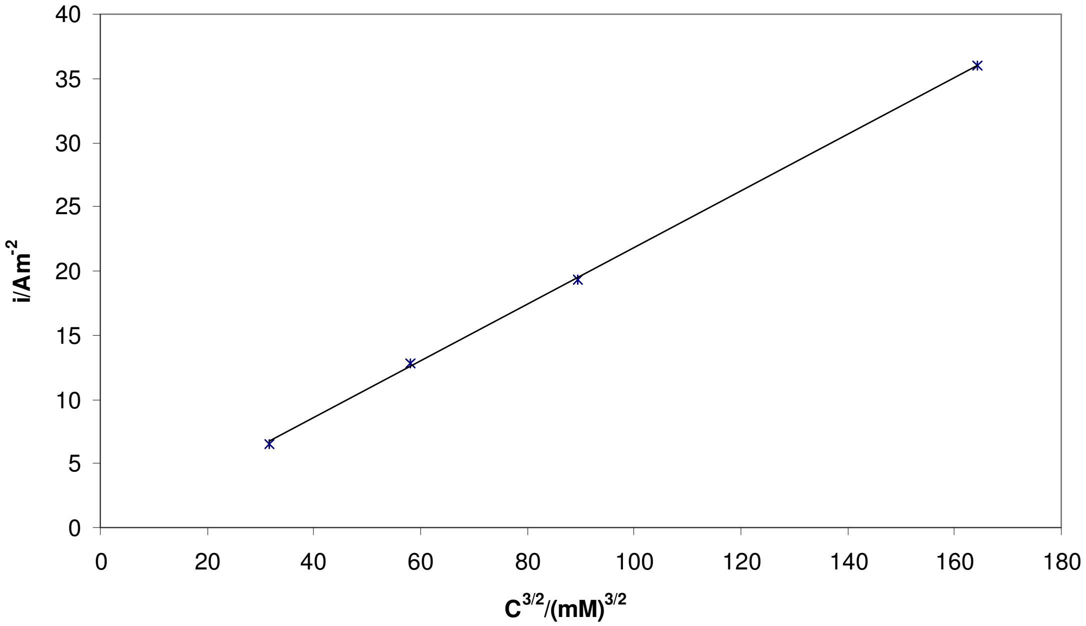

Figure 8. Current density plotted against $(C_{SO_3^{2-}})^{3/2}$. The current data are obtained after 3600 seconds in Figure 6.

As can be seen from Fig. 8 there is a good linear relationship between the current density and $(C_{SO_3^{2-}})^{3/2}$ and the linear regression line fitted to the data does pass through the origin. This result indicates that the chemical decomposition of dithionate takes place at the electrode surface and that the regenerated sulphite can be oxidised without having to be transported to the electrode surface. A similar relationship between the current and the sulphite concentration was obtained with a chronoamperometric experiment on a rotating disc electrode. The linear relationship between the current density and $(C_{SO_3^{2-}})^{3/2}$ can be used to monitor an unknown sulphite concentration in real time.

4. CONCLUSION

Chronoamperometric measurements can be used for monitoring sulphite concentrations at alkaline fresh water conditions. Both a rotating disk electrode and a wall-jet flow cell might be applicable for such measurements, but wall-jet flow cell will be better suited for industrial use. A calibrated electrode in a wall-jet flow system will therefore be useful for real-time monitoring of sulphite concentration.

The results show that in the potential area where the reaction rate is diffusion controlled there is a constant current contribution from adsorption controlled oxidation of sulphite. The constant current contribution is a function of the chemical reaction rate for the decomposition dithionate.

Chronoamperometric measurements show a linear relationship between the current density and the sulphite concentration raised to 3/2 power, $(C_{SO_3^{2-}})^{3/2}$, in alkaline electrolytes.

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