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# Effect of trace additives on the efficiency of peroxydisulfate regeneration[§]

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Direct chemical oxidation (DCO) is an emerging technology in which the organic components of hazardous or mixed waste streams are mineralized to carbon dioxide by the nearly omnivorous oxidant peroxydisulfate. Following treatment, the expended oxidant may be electrochemically regenerated to lower costs and minimize secondary waste; however, due to the varied contents of potential waste streams, trace chemical species may slowly accumulate in the system. To verify that the electrochemical recycling step was not adversely affected, the effect that several species have on the efficiency of this peroxydisulfate regeneration step has been measured. The organic additives formaldehyde, formic acid, and oxalic acid were tested, as well as the inorganic ions phosphate, nitrate, fluoride, chloride and thiocyanate. Changes in the peroxydisulfate formation potential in the presence of these additives were measured using chronopotentiometry, with current densities from 0.5 to 2.0 A cm$^{-2}$, and additive concentrations of 0.1 mM to 0.1 M. Also, a real-time technique using a rotating disc electrode was developed to measure these additives' effect on the formation kinetics of peroxydisulfate. In addition, the effect that various additives had on the rate of electrochemical peroxydisulfate generation was measured in a large-scale electrolysis cell. None of the additives caused a significant reduction in the potential or the efficiency of the peroxydisulfate generation step, although the presence of formic acid appeared to increase the efficiency. In addition, the presence of thiocyanate completely blocks the reduction of peroxydisulfate on platinum. This information is currently being applied in scale-up testing of this technology for use in treating hazardous waste or the organic components of mixed waste.

Keywords: *electrolytic*, *organic waste treatment*, *peroxydisulfate*, *trace additives*

## 1. Introduction

The remediation of organic waste by aqueous-based, nonthermal techniques is an extremely attractive goal due to the political, regulatory and public-acceptance hurdles associated with higher temperature methods, for example, incineration or molten salt oxidation. By containing the process in an aqueous phase at less than 100 °C, the potential problems of thermal runaway, release of toxic species via the gas phase or operator injury are minimized. Of the lower temperature techniques available, Direct Chemical Oxidation (DCO) [1–13] has emerged as a promising technology that is capable of nearly omnivorous mineralization of organics.

Compared with other aqueous waste treatment technologies, DCO possesses several advantages which are inherent in the chemistry of the system. First, DCO is based on the mineralization of the organic component of the waste by peroxydisulfate [14–20], one of the most powerful chemical oxidants known ($E° = +2.03$ V). Indeed, this species is the oxidant used in many laboratory total organic carbon (TOC) analysers. The combination of a powerful oxidant, a slightly elevated reaction temperature and an acidic media allows for the destruction of a wide variety of organics. Second, peroxydisulfate can be produced cleanly in an electrochemical cell from an acidified solution of ammonium sulfate, and this reaction is grounded in well-established industrial processes [21,22]. Although not required, ammonium is the cation of choice due to its exceptional solubility. This electrochemical regeneration thus minimizes the formation of secondary wastes, and improves the economics of the process. Third, the oxidant thus produced is stable for months at lower temperatures, and may be stored in large amounts until a specific waste treatment campaign is initiated. Finally, DCO is effective on a diverse group of waste matrices and is applicable to the treatment of liquids, contaminated soils or sludges, the decontamination of metal surfaces and is operable in acidic or basic media.

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Ammonium peroxydisulfate is produced electrochemically from a solution of sulfuric acid and ammonium sulfate (existing in solution as ammonium bisulfate), using a Pt anode:

$$2\,NH_4HSO_4 \Rightarrow 2\,(NH_4)_2S_2O_8 + 2\,H^+ + 2\,e^- \quad (1)$$

Oxygen is also produced at the anode and the competition between peroxydisulfate production and oxygen evolution has been well investigated [23–31]:

$$2\,H_2O \Rightarrow O_2 + 4\,H^+ + 4\,e^- \quad (2)$$

By judiciously selecting the anode reaction parameters, the current efficiency for the oxidation of sulfate to peroxydisulfate can be maximized. For the cathode reaction, the evolution of hydrogen completes the current loop:

$$2\,H^+ + 2\,e^- \Rightarrow H_2 \quad (3)$$

The anode and cathode compartments of the batch reactor cell are separated by a porous membrane in order to avoid the reduction of peroxydisulfate (back reaction of Equation 1) and consequent loss of efficiency.

The oxidant solution may then be used immediately, or stored at low temperatures ($<20\,^\circ$C) for up to several months. At higher temperatures, peroxydisulfate will slowly decompose via the reduction by water to give bisulfate and oxygen [32]. Upon initiation of waste treatment, the oxidant solution is transferred to a flow reactor (operating at 80–100 °C) and brought into contact with the waste stream. Peroxydisulfate reacts with the organic components of the waste, converting them to carbon dioxide:

$$(NH_4)_2S_2O_8 + (\text{organics}) \Rightarrow 2\,NH_4HSO_4 + (CO_2, \text{other heteroatoms}) \quad (4)$$

As the oxidant is consumed, it must be periodically renewed, and this is easily accomplished by electrolytic regeneration of peroxydisulfate from sulfate (Equation 1).

Since the oxidation of organics to carbon dioxide consists of numerous charge transfer reactions operating in series, it is possible that partially oxidized organic fragments might remain in the solution after the first pass of the waste stream through the reactor. In addition, waste streams are rarely just organic in nature and they often contain many inorganic species such as halides, nitrates, phosphates etc. These inorganic and refractory organic species will increase in concentration (at a rate which depends on the specific waste stream) unless steps are taken to periodically remove them using techniques such as ion exchange or precipitation.

Since the oxidant solution will no longer be 'virgin', care must be taken that the peroxydisulfate solution is efficiently recycled with successive use. It is important to determine before scale-up if the presence of any foreseeable species produces a detrimental effect on the peroxydisulfate regeneration process, such as an increase in the overpotential for Reaction 1, or other kinetic effects. Electricity is a significant cost of the recycling step of this waste treatment process, and small inefficiencies in terms of operating voltage can negatively impact the overall cost.

A number of researchers have studied the effect of inorganic additives on the peroxydisulfate formation reaction [23–31]. It was reported that many of these, especially the halides, cause shifts in the overpotential for sulfate oxidation due to changing charge transfer kinetics at the electrode surface. The present work expands on this previous research by measuring a wider range of additives and concentrations (including organics), and by real-time measurements of the increase in peroxydisulfate concentration in solution. Galvanostatic experiments measured the overpotential for peroxydisulfate formation, while both an *in situ* rotating disc electrode technique and tests on a larger scale cell were used to continuously monitor the electrolysis of sulfate to peroxydisulfate. No attempt was made to study short term or transient changes, as the actual peroxydisulfate waste treatment system would be run over much greater time scales, or even continuously.

## 2. Experimental details

### 2.1. *General*

Solutions were made from reagent grade chemicals and in-house distilled water. Experiments thermostated below room temperature were performed by immersing the electrochemical cell into an electronic chilled water bath. Inorganic and organic contaminants were introduced by the addition of appropriate quantities of solutions containing these moieties, ensuring that the cell solution volume change was negligible. All electrochemical measurements were made using a Princeton Applied Research (model 273A) potentiostat, controlled by PAR (model M270) software on a Pentium processor computer. Rotating disc electrode experiments were done with a PAR model 616 RDE setup with a Pt disc electrode of 0.13 $cm^2$ surface area. The electrode was polished with 1 $\mu$m alumina powder before each use. All three electrode cell potentials quoted are against an SCE reference.

### 2.2. *Chronopotentiometric experiments*

The cell setup for the constant current experiments consisted of an H-cell with 100 ml of solution in each compartment; the two sides were separated by a Nafion® 117 membrane. The solutions were made from a common stock solution of 2.65 M $H_2SO_4$ and 1.59 M $(NH_4)_2SO_4$, a solution composition used industrially in the Loewenstein process [21]. Solution temperature was 10 °C for the inorganic additive experiments, and 22 °C during the organic additive experiments. One side of the H-cell contained a carbon rod auxiliary electrode of approximately 6 $cm^2$ area. The other side contained the Pt RDE working electrode and reference. Since oxygen bubbles are also produced at the anode surface due to the electrolysis of water, the RDE was tilted slightly off-axis vertically so that these bubbles would dislodge and not block the active electrode surface. In addition, the RDE was rotated at a speed of 1000 or 1600 rpm to facilitate bubble removal; the rotation rate had no effect on the measured potential. The potential of the working electrode versus the reference was recorded for at least 10 min, as the electrode exhibited a 'conditioning' period of several minutes before attaining a constant value [23].

Chronopotentiometric experiments were done with the organic additives formaldehyde, formic acid, and oxalic acid, at concentrations from 0.1 to 100 mM. In addition, similar experiments were done with the inorganic additives fluoride, phosphate, nitrate and thiocyanate over a concentration range of 1.0 to 100 mM. For the organic additives, current densities were varied between 0.5 and 2.0 A $cm^{-2}$, chosen to represent the extremes in actual practice. For the inorganics, a nominal current density of 1.0 A $cm^{-2}$ was used.

### 2.3. *Potentiostatic monitoring of electrolysis of sulfate to peroxydisulfate*

Figure 1 illustrates the cell setup for the monitoring of peroxydisulfate formation from the bulk electrolysis of sulfate. This setup is a modification of that described in reference [23]. A dc power supply (max. output 10 A at 40 V) was used to generate peroxydisulfate in the anode compartment of an H-cell (Equation 1). The anode consisted of a Pt strip, masked off with Teflon tape to expose 2.3 $cm^2$ of surface, while the cathode (in the opposite compartment of the H-cell) was a carbon rod of area 6 $cm^2$. The current density was typically 1.0 A $cm^{-2}$ at the anode, and the voltage necessary to produce this was about 15 V. Situated in the same compartment as this anode, a platinum rotating disc electrode (poised at −0.1 V by the potentiostat) was used to monitor the increase in peroxydisulfate generated in this cell compartment by measuring its reduction current:

$$S_2O_8^{2-} + 2\,H^+ + 2\,e^- \Rightarrow 2\,HSO_4^- \qquad (5)$$

The Pt RDE was rotated at a speed which was sufficient to continuously dislodge any hydrogen bubbles which formed on the surface due to the electrolysis of water. Oxygen bubbles also accumulated at the RDE due to the close proximity of the Pt strip anode driven by the power supply, at whose surface peroxydisulfate and oxygen were being generated. The initial solution composition in the H-cell before electrolysis was the same as for the galvanostatic experiments described above, 2.65 M $H_2SO_4$ and 1.59 M $(NH_4)_2SO_4$. Solution temperature was 10 °C for the inorganic additive experiments, and 22 °C during the organic additive experiments. Care was taken that the reference for the potentiostat did not lie directly in the electric field generated across the electrodes of the d.c. power supply, as unstable readings resulted.

A typical bulk electrolysis experiment was of at least an hour duration. Upon the start of the experiment, the potentiostat (controlling the RDE) was connected and a background current measured. This background current was due to the reduction of dissolved oxygen, and degassing the solution with nitrogen eliminated this current. After 2 min, the power supply was connected and the current was adjusted to either 2.30 A (1.0 A $cm^{-2}$) or 0.230 A (0.10 A $cm^{-2}$), measured with a digital multimeter. A blank run was done in the absence of any organic additives; subsequent runs were run in an identical fashion except that the solution on the anode side of the cell contained a fixed concentration of a particular organic. For the experiments with inorganic additives, the duration of the experiment was increased and aliquots of solutions containing the potassium or sodium salts of the inorganic moieties were introduced at fixed times during the run. The additives were the same as with the potentiometric experiments described above, with the addition of chloride ion.

### 2.4. *Large-scale electrolysis cell*

Figure 2 depicts the electrolysis cell used for tests on the oxidation of sulfate to peroxydisulfate. The cell consisted of either three or six platinum anodes op-

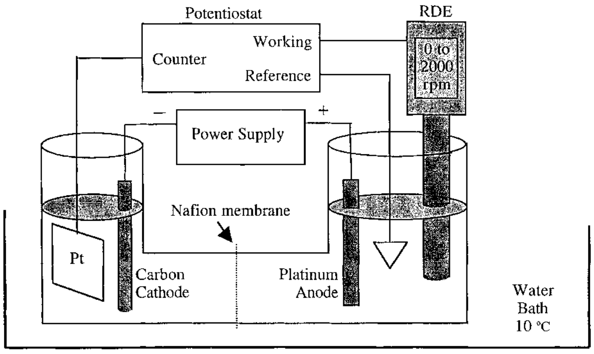

Fig. 1. Schematic diagram of the experimental setup for production and real time monitoring of peroxydisulfate.

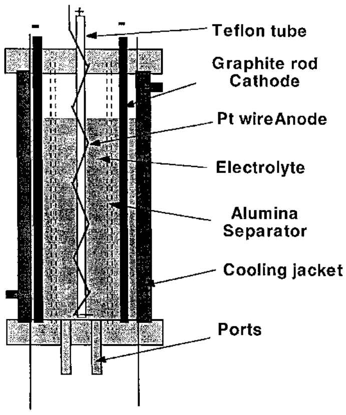

Fig. 2. Schematic of 100 A electrolyser for production of peroxydisulfate.

erating in parallel with six graphite rod cathodes. Each water-cooled anode unit consisted of platinum wire (dia. 0.051 inch) wound around a cooling tube. All experiments were conducted using a suitable d.c. power supply operating at a fixed total current of 100 A with cell voltages between 6 and 10 V. Anode current densities were either 0.4 or 1 A cm$^{-2}$ depending on the number of anodes. The high specific amperage (80 A dm$^{-3}$) is typical of industrial cells [21,22] and sufficiently large to minimize the extent of the chemical reduction of peroxydisulfate in the vicinity of the platinum anode. Although an electrolysis temperature of 10–15 °C was desired, the actual operating temperature was 25 °C due to ohmic heating of the solution.

Solutions of 2.4 dm$^3$ total (equally divided between anolyte and catholyte) of acidified ammonium sulfate (2.65 M $H_2SO_4$ + 1.59 M $(NH_4)_2SO_4$) were electrolysed for up to 2 h. The baseline, or control, solution consisted of this sulfuric acid/ammonium sulfate solution with the additives normally used in industrial cells: 7.8 × 10$^{-3}$ M ammonium nitrate and 3.4 × 10$^{-3}$ M potassium thiocyanate. To this baseline solution was added chloride, nitrate, or phosphate to make 0.05 M solutions of these ions. During electrolysis, 1.0 ml of solution was taken every 15 min over a period of up to 2 h. The solution was diluted and reduced with 0.1 N Fe(II) solution, and then back titrated with a standardized solution of $KMnO_4$ until the colour-determined endpoint. Approximately 5 min was allowed for the total oxidation of Fe(II) by peroxydisulfate because this reaction is slow at room temperature.

## 3. Results and discussion

### 3.1. *Chronopotentiometry*

Under the electrolysis conditions used in the generation of peroxydisulfate, the electrolysis of water at the anode of the cell is thermodynamically more favourable than the oxidation of sulfate to peroxydisulfate [33]. Fortunately, kinetic limitations suppress the oxygen evolution reaction so that generation of peroxydisulfate at current efficiencies of up to 80% at Pt electrodes can be achieved [23]. This kinetic competition between oxygen and peroxydisulfate production is very sensitive to the exact nature of the electrode/electrolyte interface; for example, platinum is one of the few electrode materials which can generate peroxydisulfate from acidic sulfate solutions. Under constant current conditions, a shift in the relative rates of the two competing reactions would be immediately apparent by a change in the required potential. The chronopotentiometric experiments described were done to insure that the presence of various organic and inorganic species in solution did not promote the oxygen evolution rate at the expense of the sulfate oxidation reaction.

Of course, any organic moieties added to the system will be rapidly oxidized by the peroxydisulfate generated at the electrode, and in a long-term sense they are not really present. The organic additives chosen for this study are either refractive species [7] or likely intermediates along the oxidative pathway for nearly all organics. Abundant references exist on the adsorption of various species onto electrode surfaces, and organic species on platinum electrodes is no exception (CO poisoning of platinum, for instance). In addition, intermediates formed en route to the final product (carbon dioxide) may also adsorb onto the electrode surface and perturb the ratio of oxygen to peroxydisulfate generation. With the exception of chloride, the inorganic species studied are not oxidizable under the conditions described and will persist in their initial form in solution. Chloride ion is oxidized to chlorine gas, and possibly higher valency states. The adsorption of any of these inorganics onto the electrode might also reduce the efficiency of the peroxydisulfate regeneration process.

A typical chronopotentiometric experimental result is shown in Fig. 3. Upon connection of the potentiostat and flow of a set current (at $t = 0$ s), the working electrode potential rapidly increases for approximately one minute. This potential shift is indicative of an electrode conditioning period, and has been noted before [23]. Evidently, the establishment of a particular oxide surface layer structure on the platinum is necessary for the favouring of the peroxydisulfate generation reaction over that of oxygen evolution. After the conditioning period, the potential remained relatively constant for the duration of the experiment. Scatter can be seen in the results, presumably due to interfacial perturbations caused by bubble formation at the electrode surface. This noise was greater the higher the current density.

Raw data such as that of Fig. 3 were collected for the matrix of additive, concentration, and current density, and the reduced data are shown in Table 1. The average potential recorded over the duration of an individual run (not including the conditioning period, as well as the standard deviation from this potential, is given. For the entire matrix of additive types, concentrations, and current densities, the av-

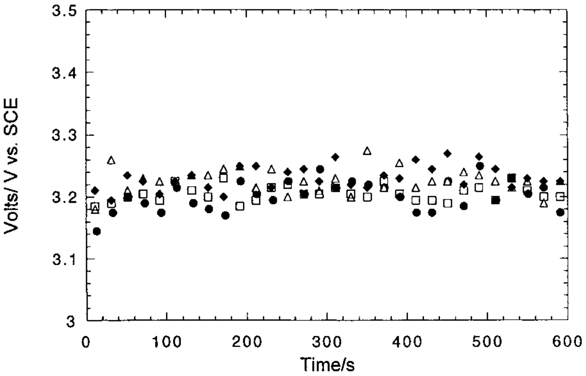

Fig. 3. Chronopotentiometry of 2.65 M $H_2SO_4$ and 1.59 M $(NH_4)_2SO_4$ solutions at a platinum anode with and without 10 mM organic additives added. Current density was 1.0 A cm$^{-2}$. Organic additives: (●) no additive, (△) HCHO, (◆) HCOOH, (■) $(COOH)_2$.

*Table 1. Average Pt anode potential recorded during chronopotentiometric experiments for listed additives and current densities*

Additive concentrations were 0.1 M
Standard deviations are in the potential for an individual run

| | Current density | | | | | |
|---|---|---|---|---|---|---|
| | $0.5\ \mathrm{A\ cm^{-2}}$ | | $1.0\ \mathrm{A\ cm^{-2}}$ | | $2.0\ \mathrm{A\ cm^{-2}}$ | |
| *Additive* | *Potential* /V vs SCE | $\sigma$ | *Potential* /V vs SCE | $\sigma$ | *Potential* /V vs SCE | $\sigma$ |
| None | 2.932 | 0.060 | 3.208 | 0.042 | 3.719 | 0.079 |
| HCHO | 2.935 | 0.038 | 3.200 | 0.038 | 3.655 | 0.075 |
| HCOOH | 2.955 | 0.041 | 3.218 | 0.021 | 3.679 | 0.078 |
| $(\mathrm{COOH})_2$ | 2.896 | 0.042 | 3.196 | 0.019 | 3.721 | 0.079 |
| $\mathrm{F^-}$ | | | 3.255 | 0.035 | | |
| $\mathrm{NO_3^-}$ | | | 3.252 | 0.047 | | |
| $\mathrm{PO_4^{3-}}$ | | | 3.220 | 0.037 | | |
| $\mathrm{SCN^-}$ | | | 3.238 | 0.037 | | |

erage potential for a particular run fell within the standard deviation of the potentials observed with no additive. Table 1 lists only the results for the highest additive concentration studied; lower additive concentrations produced even smaller differences in electrode potential. Thus, over the experimental conditions studied, no significant changes in the working electrode potential due to the additives' presence were observed.

### 3.2. In situ *monitoring of peroxydisulfate formation*

Chronopotentiometric experiments such as described above provide a partial answer to the study of additive effects by providing information as to the relative rates of the competing anode reactions. However, a more absolute measure would be to measure the effect that an additive has on the real-time rate of peroxydisulfate generation. As described in Section 2, a rotating disc electrode setup was used to monitor the increase in peroxydisulfate concentration, while the peroxydisulfate was being generated in the same cell by a separate pair of electrodes. The RDE was biased at a potential where peroxydisulfate is reduced (Equation 5), and the measured reduction current was demonstrated to be indicative of the bulk concentration of peroxydisulfate in solution. This experiment was repeated in the presence of additives, and any changes in the rate of peroxydisulfate production were noted.

Although the thermodynamic potential for the sulfate/peroxydisulfate couple in acidic solution is +2.123 V, the overpotential for the reduction of peroxydisulfate at a platinum electrode is substantial. Significant current for this reaction was not observed until the electrode potential was negative of 0 V vs SCE. However, the electrolysis of water commenced negative of −0.2 V and the associated formation of hydrogen bubbles precluded consistent reduction currents for peroxydisulfate. Through trial and error, it was determined that the optimum potential for the reduction of peroxydisulfate at platinum using this method was between −0.1 and −0.2 V.

For a system with rapid rates of electron transfer, the faradaic current at a rotating disc electrode will be governed by the flux of reactant to the electrode surface [34]. The Levich equation can be used to relate the current to the electrode rotation speed; a plot of this nature for peroxydisulfate is shown in Fig. 4. The data in this plot approach linearity, which is indicative of the current being governed solely by mass transport. In addition, if the system is in the limiting current regime, the current will be proportional to the bulk concentration of the reactant. This was confirmed for the peroxydisulfate reduction, and the correlation between reduction current and concentration is shown in Fig. 5. The experiments were repeated numerous times, and the repeatability was found to be within ±10%. It was also determined that the presence of the inorganic and organic additives studied did not affect the peroxydisulfate reduction current. Thus, this RDE measurement provides a relatively quick determination of the concentration of peroxydisulfate in solution.

This technique was used to monitor the kinetics of peroxydisulfate formation in two separate types of experiments, with both experiments having the same

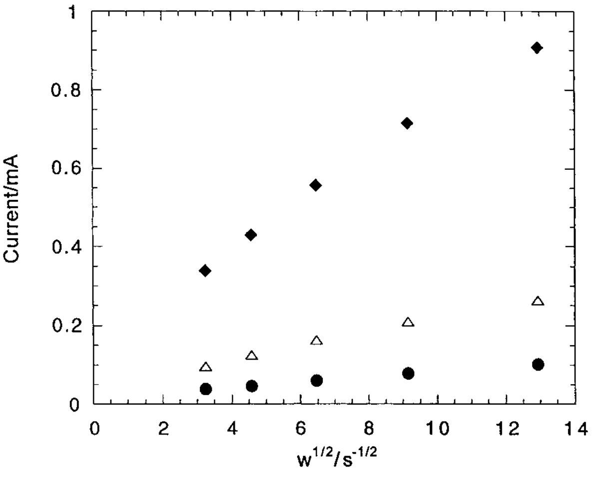

Fig. 4. Levich plot of peroxydisulfate reduction at Pt RDE. Solutions were 2.65 M $H_2SO_4$ with added $(NH_4)_2S_2O_8$. (●) 2.0 mM $(NH_4)_2S_2O_8$, (△) 5.0 mM $(NH_4)_2S_2O_8$, (◆) 20 mM $(NH_4)_2S_2O_8$.

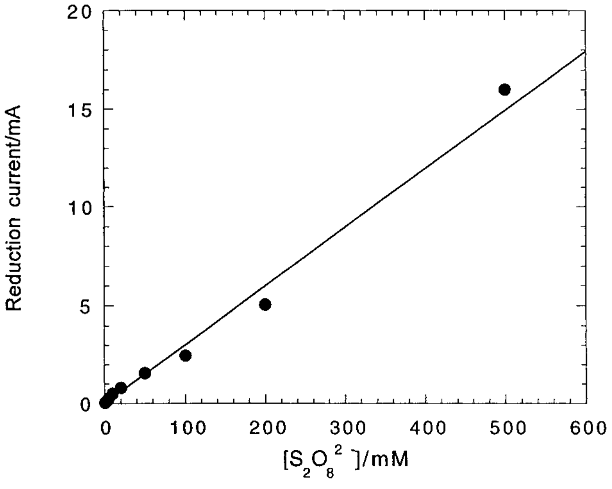

Fig. 5. Plot of reduction current against peroxydisulfate concentration. Pt RDE at 1600 rpm potential at −0.2 V in a solution of 2.65 M $H_2SO_4$ with added $(NH_4)_2S_2O_8$.

general conditions. In the first type of experiment, runs were done with no additives and compared with identical runs done in the presence of a particular organic additive. In the second type, increasing aliquots of a given inorganic additive were added to runs already underway and any effect on the peroxydisulfate production rate was noted. The runs with no additives were identical in both cases; an example of such a run is shown in Fig. 6.

In all the runs such as shown in Fig. 6, it was observed that the concentration of peroxydisulfate increased in a near-linear fashion. Eventually, the current would taper off due to the depletion of sulfate from the anolyte, but the electrolysis times and currents were chosen to lie within the linear region. A short conditioning period was noted in the first few minutes, and is most likely the same behaviour as seen in the chronopotentiometric experiments. Numerous runs were done with all of the additives, and the results are presented in Table 2. For each additive, the rate of production of peroxydisulfate is listed. The observation that the peroxydisulfate formation rate for the inorganic series blank is higher than that for the organic series is no doubt due to the fact that the former experiments were done at a lower, and hence more efficient, temperature.

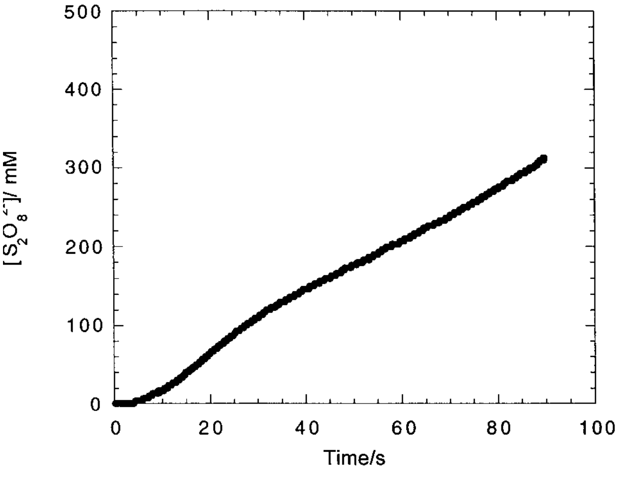

Fig. 6. Plot of peroxydisulfate concentration against time for electrolysis of 2.65 M $H_2SO_4$ and 1.59 M $(NH_4)_2S_2O_4$ at 25 °C in small-scale cell.

*Table 2. Peroxydisulfate production rate in the presence of the additives studied*

| *Additive* | $S_2O_8^{2-}$ *formation rate* /mol $h^{-1}$ | *Variance* /mol $h^{-1}$ |
|---|---|---|
| Organics | | |
| blank | 0.018 | ±0.001 |
| HCHO | 0.018 | ±0.001 |
| HCOOH | 0.030 | ±0.002 |
| oxalic acid | 0.018 | ±0.001 |
| Inorganics | | |
| blank | 0.025 | ±0.002 |
| $NO_3^-$ | 0.024 | ±0.002 |
| $F^-$ | 0.026 | ±0.002 |
| $Cl^-$ | 0.025 | ±0.002 |
| $SCN^-$ | see text | – |

For the organic additives formaldehyde and oxalic acid, virtually no difference was seen in the rate of production of peroxydisulfate. As was the case in the chronopotentiometry, this result is not unexpected because the large excess of peroxydisulfate would be expected to immediately mineralize the additive. However, for the experiment done in the presence of formic acid, this rate appeared to be substantially higher. This result was quite reproducible and the increased rate was observed throughout the course of the experiment. As the additive concentration is but a fraction of that of peroxydisulfate, it is likely that this observation is due to a surface electrode effect; one possible scenario is the diminishment of active sites for oxygen evolution. Nevertheless, for the purposes of the DCO organic waste treatment technology, the effect is not detrimental.

None of the inorganic additives had any effect on the peroxydisulfate generation rate, although a definite answer was not possible for thiocyanate due to a measurement idiosyncrasy. Upon the addition of this ion at a specified interval into the experiment, the reduction current measured at the RDE immediately fell to background levels. Up until the thiocyanate addition, the RDE reduction current indicated that peroxydisulfate was being generated at the same rate as in the other experiments. This fact, along with the chronopotentiometry results for the thiocyanate additive, point exclusively to the conclusion that thiocyanate does not block the production of peroxydisulfate but rather blocks its reduction at a platinum electrode. The electrochemistry of thiocyanate at platinum anodes has been investigated [35–37] and indeed, adsorption of thiocyanate and its oxidation products has been observed at platinum [36–38] and other electrode surfaces [39].

### 3.3. *Large scale electrolysis cell*

Using the electrolysis cell shown in Fig. 2, the buildup of peroxydisulfate is plotted against time for

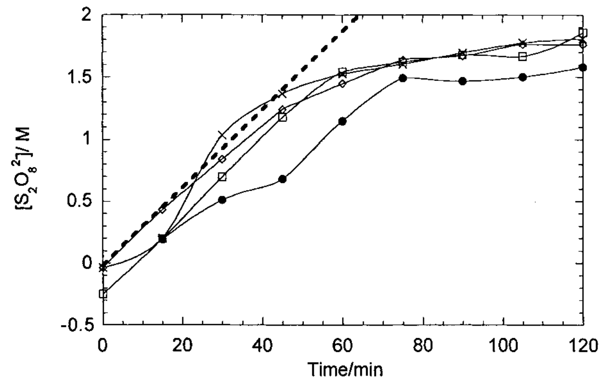

Fig. 7. Electrolysis of ammonium sulfate at low current density (0.4 A $cm^{-2}$) of acidified sulfate solution with no additives (●), and with 0.05 M amounts of chloride (□), phosphate (◇), and nitrate (×). Broken line is for current efficiency of 80%.

fixed currents of 100 A and fixed anolyte volumes (1.2 $dm^3$). Figure 7 illustrates the results at a cell current density of 0.4 A $cm^{-2}$ while Fig. 8 gives the data obtained at 1.0 A $cm^{-2}$. Occasional negative values of oxidant are likely the results of reduced accuracy of the back titration technique (Section 2) at very low oxidant concentrations. In all cases, the best reported industrial efficiencies of 80% are found at sulfate concentrations up to 1.5–2 N, depending on current density and temperature. Limitations in the capacity of the cooling system (which effected a stable operating temperature of 25 °C at the high current density) prevented chilling this solution to 14 °C where higher steady state peroxydisulfate concentrations would be expected. However, in neither experiment at low and high current densities was there a clear deterioration of peroxydisulfate generation efficiency due to the presence of chloride, phosphate or nitrate.

### 3.4. *Coulombic efficiency*

Since the anode process in this system is a competition between oxygen evolution and peroxydisulfate production, the coulombic efficiency for the production of the latter is a useful barometer of the efficiency of the process. Coulombic efficiencies are easily calculated for the experiments with and without additives, as the theoretical production rate of peroxydisulfate can be compared with the actual production rate measured by the RDE technique. Stated another way, the plot of oxidant concentration against time can be related to current efficiency, *e*, through a variation of Faraday's law:

$$e = \frac{[\mathrm{Ox}(t)]V_\mathrm{a}}{(It/F)} \tag{6}$$

This efficiency is simply the ratio of equivalents of oxidant formed in solution of volume $V_\mathrm{a}$ to the charge passed expressed in equivalents through the Faraday constant, F (96 500 C $equiv^{-1}$). For the small scale RDE experiments described above (shown in Fig. 1), calculated coulombic efficiencies were about 50%. This is somewhat lower than the 70 or 80% that has been obtained in industrial process [21,22], but this may be due to the particular operating parameters chosen for the present experiments. On the other hand, coulombic efficiencies of up to 80% were achieved in the present work with the large-scale electrolysis cell (Fig. 2) due to the different densities, cell configuration etc.

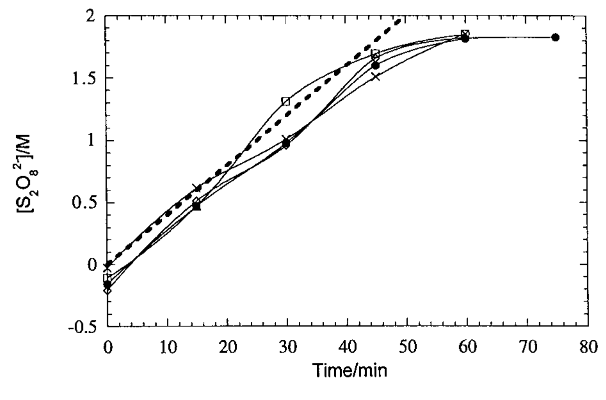

Fig. 8. Electrolysis of ammonium sulfate at low current density (1.0 A $cm^{-2}$) of acidified sulphate solution with no additives (●), and with 0.05 M amounts of chloride (□), phosphate (◇), and nitrate (×). Broken line is for current efficiency of 80%.

Although it appears that none of the additives studied had a detrimental effect on peroxydisulfate production, several caveats must be mooted. First, the tests were on the order of several hours duration, while an actual waste processing system might run for much longer times, or even continuously. However, if the additives were to perturb the electrode/electrolyte interface, the effect would almost certainly be observed immediately. Second, no attempt was made to study the effect of more than one additive at once. Finally, the conclusions are limited strictly to the additives studied; other species are possible, albeit less likely. These last two points are difficult to address because predicating *a priori* what might be present in the oxidation electrolysis system is extremely difficult due to the complex nature of possible waste streams.

## 4. Conclusions

Direct chemical oxidation is a promising technique for the mineralization of organic waste streams through the use of peroxydisulfate, and a significant advantage of this technique is the minimization of secondary waste streams through electrolytic regeneration of this oxidant. However, it must be insured that organic and inorganic moieties present during the oxidant regeneration step do not adversely affect the efficiency of the process. In the series of chronopotentiometric experiments described here, it was determined that the presence of the refractory organics formaldehyde, formic acid, oxalic acid, and the inorganic ions phosphate, thiocyanate, nitrate, chloride and fluoride had no measurable effect on the overpotential for the sulfate to peroxydisulfate oxidation.

An electrochemical method for the real time measurement of peroxydisulfate solution concentration was developed, and this technique was used to measure the effect that the above additives had on the kinetics of the sulfate to peroxydisulfate reaction. Again, no detrimental effect on the rate was noted, although the presence of formic acid appeared to increase the rate. In addition, the presence of thiocyanate ion was found to completely block the reduction of peroxydisulfate to sulfate, and it was not possible to measure the peroxydisulfate generation rate in this particular system. Experiments done with a larger scale system which more closely mimicked an actual industrial system again showed that these additives had no effect on the efficiency of the electrolysis of sulfate to peroxydisulfate.

These results are being incorporated into design considerations for a scaled up version of this waste remediation technology at Lawrence Livermore, and the system will be tested on actual waste streams. Further aims are the application of this technology to the destruction of specialized waste streams, such as chemical warfare agents, chlorinated solvents, and contaminated sludges and soils.

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