DEVELOPMENT OF ELECTROCHEMICAL OXIDATION USING DIAMOND - COATED ELECTRODES FOR THE TREATMENT OF WASTE LUBRICANTS: PART 1 ASSESSMENT OF POTENTIAL

G.T. Taylor, A.W.E. Newey
AWE
Aldermaston, Reading, RG7 4PR, UK.

ABSTRACT

Electrochemical oxidation using electrodes coated with boron-doped diamond is a potential treatment process for waste oils contaminated with radioactive materials. If it could be applied to destroy the waste oils without resorting to the use of aggressive chemicals, it would facilitate the disposal of the radioactive contaminants. Accordingly AWE has examined the oxidation of various non-radioactive oils in a laboratory scale electrochemical cell equipped with diamond-coated electrodes with the objective of initiating the development of a disposal process.

Before starting the experimental work with the oils, the equipment was commissioned with sucrose. Oxidation of at least 98% of the added sucrose was achieved. The current efficiency for the oxidation depended on the sucrose concentration. It was concluded that the rate of oxidation was limited by the applied current at high concentrations and by the rate of sucrose diffusion at low concentrations. The electrodes were found to lose their diamond coating during operation, but this did not appreciably affect the oxidation of sucrose.

The process was capable of oxidising an aqueous emulsion of a cutting oil, but mineral oils resisted oxidation. It was thought that this might have been due to a poor contact between the oil suspended in the electrolyte and the electrode surface. Accordingly, a surfactant system was devised to emulsify the mineral oils, but this did not lead to a significant improvement in performance. When sucrose was added to the electrolyte containing an emulsified mineral oil, the oxidation of the sucrose was inhibited. This indicated that there could be some property of the emulsified mineral oil that inhibits the electro-oxidation of its organic components. Further work is required to understand the system before the process can be developed. It is expected that the activity of the electrodes will be influenced by the loss of the diamond coating, and that successful development of the technology will require a supply of stable electrodes.

INTRODUCTION

AWE (formerly known as the Atomic Weapons Establishment) is investigating possible methods to treat waste oils contaminated with radioactive materials (e.g. immobilisation in cement and biodegradation [1]). Electrochemical oxidation with diamond-coated electrodes is a promising new technology that has the potential to destroy organic materials without the use of aggressive chemicals [2, 3]. Application of the technology to waste oils from radioactive applications would transfer the radioactive materials to an aqueous environment, so facilitating disposal or recovery.

A feasibility study showed that the process was able to oxidise a cutting oil (Solcut BR) to carbon dioxide [4], although a hydraulic oil resisted oxidation. Consequently, AWE purchased a laboratory scale rig to fully evaluate the potential of the technology. The objective was to devise a procedure for destroying minerals oils and thus initiate the development of the process for the disposal of waste oils. This paper presents the results of this work, which employed non-radiologically contaminated oils.

Equipment, Materials and Methods

The diamond-coated electrodes were supplied by Condias, Fraunhofer Strasse, Itzehoe, Germany. They were manufactured by chemical vapour deposition onto a niobium substrate using methane as the source of the carbon for the diamond, and diborane as the source of the boron. The electrodes were arranged as a set of 5 plates separated by PTFE spacers that were held in a cylindrical electrochemical cell. The dimensions of the electrodes were 350 mm high x 45 mm wide x 2 mm thick, giving a nominal electrode area of 1000 cm^2. There were 3 anode plates separated by 2 cathode plates [4]. The current was provided by a 20 Volt, 50 Amp power supply that was capable of continuous independent voltage and current variation up to 20 Volts and 50 Amps.

Batch operation was employed, using an electrolyte that contained the test organic compound and 10 g/l $Na_2SO_4.10\ H_2O$ in demineralised water. The electrolyte was recirculated at 60 litres/hour through the electrochemical cell to a 20 litre capacity reservoir tank by a positive displacement pump. The volume of electrolyte was 7.5 litres unless shown otherwise. The temperature of the electrolyte was not controlled, and it generally reached 35 – 50 ^{o}C (the exact value being determined by ambient temperature and current).

The sources of the test compounds were:

Sucrose	food grade sugar
Solcut BR	Houghton Vaughan (although this cutting oil is no longer manufactured). Solcut BR was formulated with severely refined mineral oil, petroleum sulphonates, potassium salts of tall oil, oleate ester of polyethylene glycol, xylenol rich cresylic acid and a trace of antifoam.
OM33, OM80, OMD81 oils	Esso
Tellus R10 oil	Shell
Brillo detergent	Johnson Wax Professional
Atlas and Brij surfactants	Uniquema (formerly ICI Surfactants)

The headspace above the liquid in the electrochemical cell and electrolyte reservoir tank was purged with air. The flow rate was 15 litres/minute unless shown otherwise. The carbon dioxide content of the off-gas was measured by passing part of the gas stream through a Guardian infrared carbon dioxide meter manufactured by Edinburgh Instruments, Livingston, UK. The detector was calibrated at intervals using pure nitrogen and nitrogen containing 0.5% v/v carbon dioxide. The amount of carbon dioxide liberated by electrolysis was calculated from the measured concentration of carbon dioxide and the air flow rate, making an allowance for the content of carbon dioxide in the atmosphere. However, the system broke-down on several occasions. This was often caused by leaks in the meter’s internal pump and in the gas line to the detector. It was thought possible that oxidants were carried over in the off-gas stream and that they caused the rubber in the pump and gas line to perish. Nevertheless, the carbon dioxide meter gave useful data, and it provided a means of measuring the extent of oxidation that was independent of the analysis of the amount of organic material in the electrolyte.

The amount of organic material in the electrolyte was monitored via its Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) content. Samples were taken periodically during the course of each run and analysed using Dr Lange test kits (LCK014, LCK114 and LCK314 for COD; LCK381 and LCK 380 for TOC) and a LASA20 photometer.

Wherever possible, the carbon mass balance was calculated during a run from the TOC of the electrolyte and the amount of carbon released as carbon dioxide in the off-gas. However, it was often difficult to take a representative samples during the tests with Solcut BR and the emulsified oils, particularly if a significant amount of oil had separated from the emulsion. This caused wide variations in the values of the COD and TOC analysis, and the results were not used in the evaluation when this occurred.

The current efficiency for the oxidation of sucrose was calculated by comparing the measured decrease in COD to that expected from the charge passed. The electrochemistry of the oxidation at the anode is:

$$2H_2O \rightarrow 4H^+ + 2[O] + 4e^-$$

$$2[O] + \text{organics} \rightarrow mCO_2 + nH_2O$$

Thus, the loss of 2 gram atoms of COD, i.e. 32g oxygen demand, involves 4 moles of electrons. One mole of electrons is equivalent to 1 faraday, which equates to 96479 coulombs, i.e. 96479 Amp.seconds.

Therefore, with a 100% current efficiency, passing a current of 1 Amp for 1 second should reduce the COD by

$$32 / (4 \times 96479) \quad = \quad 8.29 \times 10^{-5} \quad \text{grams oxygen demand.}$$

Results and Discussion

The aims of the work reported here were to confirm that Solcut BR cutting fluid was readily oxidised (as shown by the feasibility study [4]) and to devise a procedure for destroying minerals oils. Before starting this experimental work, the operation of the equipment was checked by examining the oxidation of sucrose. The runs with sucrose also gave some understanding of the principles underlying the oxidation. Furthermore, when it was seen that the electrodes were losing their diamond coating, sucrose oxidation was used to check the oxidative performance of partially delaminated electrodes.

Electrode Stability

Loss of the diamond coating (Figure 1) was observed during the trials with 3 different sets of electrodes. It was expected that the niobium substrate would form a passive, insulating oxide film, so that the loss of coating would have the effect of reducing the active surface area of the electrodes. Delamination was observed from the start of operation. It affected the anodes more than the cathodes, and it tended to commence at the sides and corners of the electrodes and then spread to the face. The nature of the delamination is illustrated in Figure 1 for the third set of electrodes after 11,000 Amp.hours of operation

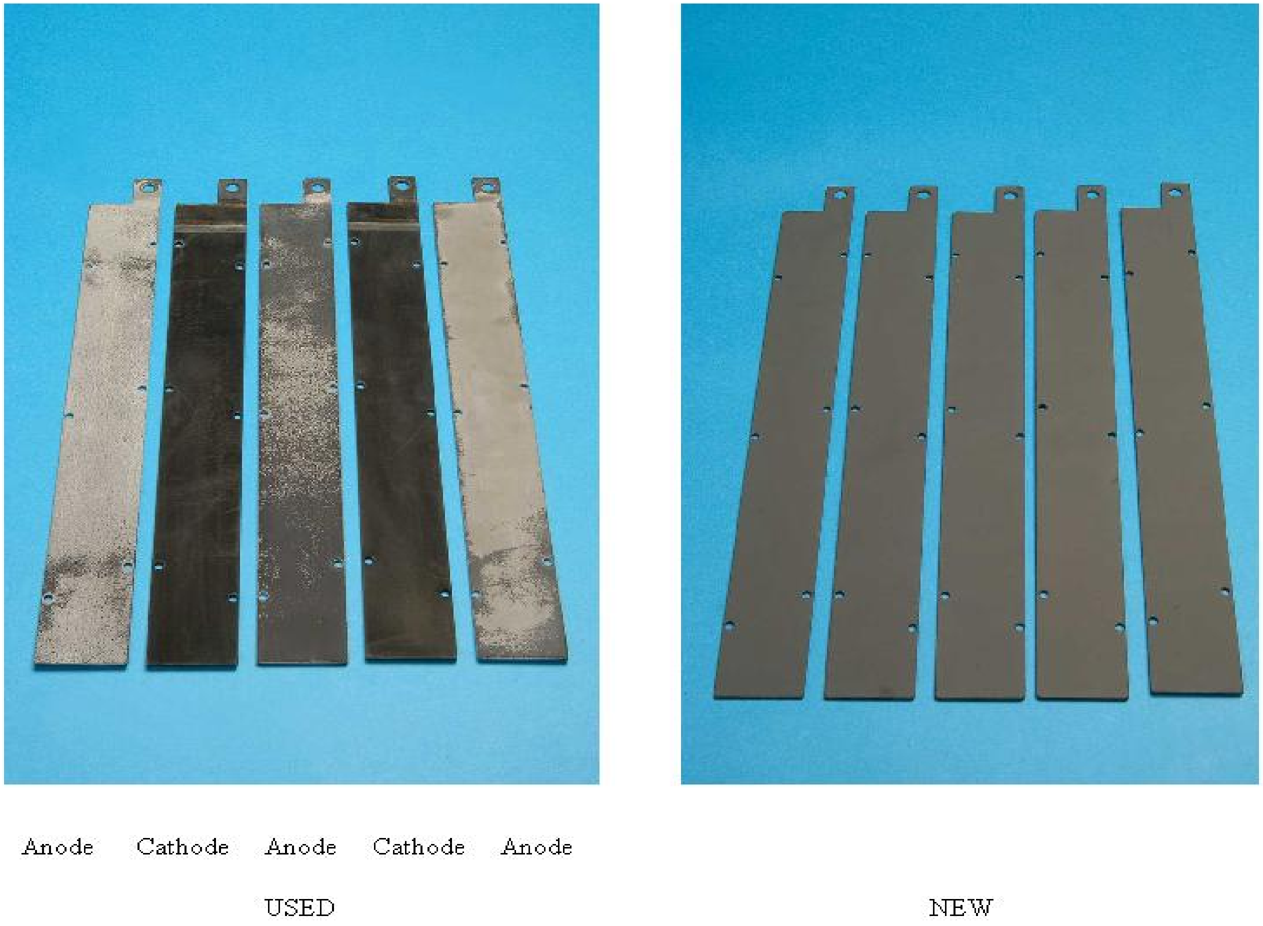

Fig. 1. Appearance of used and new electrodes

The appearances of the anodes and cathodes were markedly different. The anodes had developed light coloured patches, characteristic of delamination. By contrast, the cathodes had become darker. The only region on the cathodes showing possible delamination was a band at the liquid surface. Moreover, there were differences in the appearance of the 3 anodes. The 2 faces on the outside of the electrode stack were lined as if the delamination had occurred in streaks. In addition, the 2 faces of the central anode were different: one face showed nearly complete delamination: the other showed much less delamination, and this was restricted mainly to the central area. Delamination had also occurred on the inner faces of the holes in the anodes that accommodated the PTFE spacers, even though these holes had been covered by the spacers.

Oxidation of Sucrose

The apparatus installed at AWE [4] was commissioned by carrying out 2 oxidation runs with sucrose. These confirmed that the apparatus was functioning correctly. In the first run, which employed a concentration of 1 g sucrose per litre and a current of 12 Amps, the TOC decreased by 72 %, and the COD decreased by 78 % over 8.8 hours (Table I).

There was a greater degree of oxidation when the concentration of sucrose was increased to 4 g per litre in the next run: approximately 99 % of the sucrose was oxidised (as shown by COD - Figure 2).

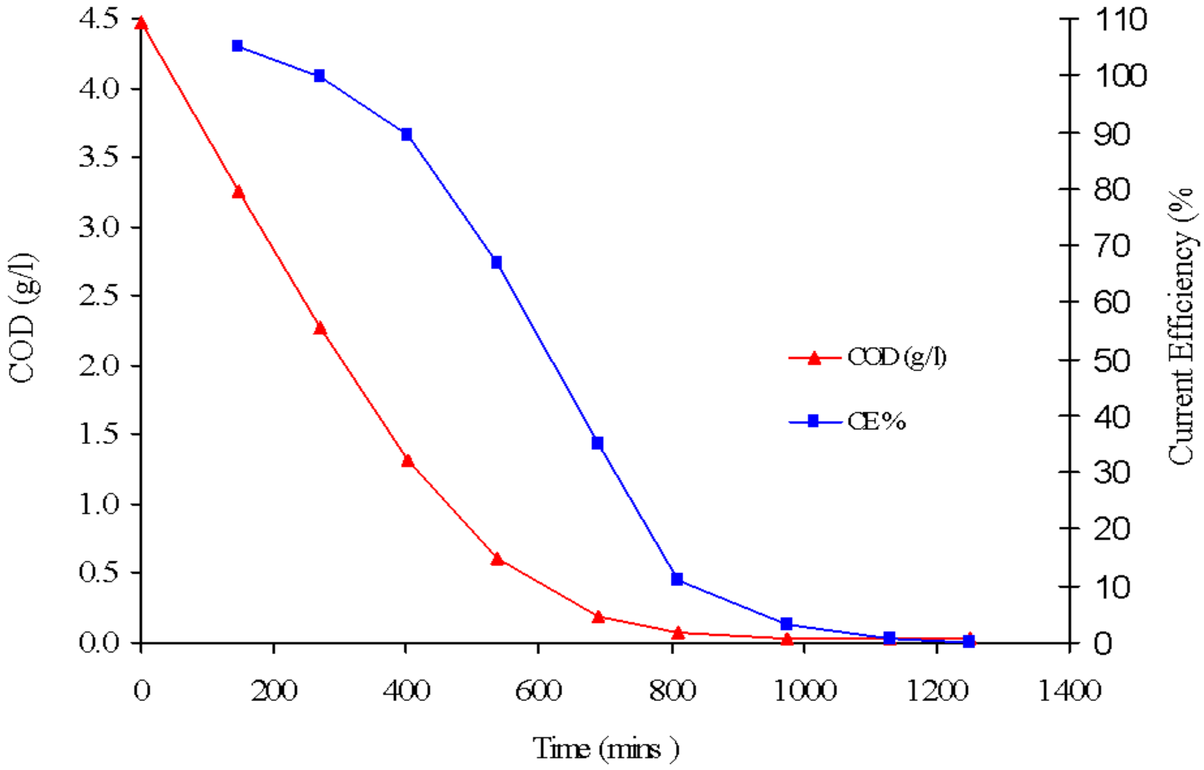

Fig. 2. Oxidation of sucrose

Table I. Oxidation of Sucrose

Set of Electrodes		First		Third		
Cumulative Usage at Start of Run (Amp.hours)		<50	<150	<10	1430	12,200
Run Time (hours)		8.83	20.8	17	19.5	22
Current (Amperes)		12	12	24	24	24
Initial [Substrate] (grams/litre)		1	4	8	8	8
Removal of	TOC	72 %	not determined	99.8 %	97.8 %	98.2 %
	COD	78 %	99.4 %	99.8 %	98.7 %	99.1 %
Initial Amount of Organic Carbon (grams)		6.32 [a]	25.3 [a]	25.3	25.3	25.3
Max. Concentration of Generated CO_2 in Outlet Gas (% v/v)		not determined	not determined	1.15	0.73	0.81
Amount of Carbon Liberated as CO_2 (grams)		not determined	not determined	19.4	21.6	17.8

[a] Volume of electrolyte = 15 litres, air flow = 10 litres/min

It was noted that the initial rate of oxidation was linear. The corresponding current efficiency during the initial phase was approximately 100 % (Figure 2). During the latter phase, the current efficiency decreased and the rate of loss of COD became approximately exponential. This behaviour can be explained in terms of the mechanism of the electro-oxidation. The rate of oxidation was initially be limited by the rate at which the electrons were removed from the organics, i.e. it was limited by the current. The oxidation reactions are thought to occur at or very close to the surface of the electrode [5]. As the sucrose concentration fell during the course of the run, the rate of oxidation became limited by the rate at which the sucrose could diffuse to the electrodes. The transition with sucrose under these conditions occurred at about 1.5 g COD/litre.

The oxidation of sucrose was not tested with the second set of electrodes. The third set was as effective with sucrose as the first set. The initial concentration of sucrose was increased to 8 g / litre and the current was increased to 24 Amps in proportion (Table I). The third set of electrodes produced a high degree of oxidation (98 – 99% as measured by removal of TOC and COD). The degree of oxidation indicated by carbon dioxide production was not as high as that indicated by the decrease in TOC and COD. The amount of carbon measured in the outlet gas as carbon dioxide was less than expected from the added amount of sucrose. It was considered that the measurement of TOC and COD gave a more accurate reflection of the degree of oxidation than did the calculation of the amount of carbon lost as carbon dioxide, because of the errors in measuring air flow and carbon dioxide concentration.

It was noteworthy that the degree of oxidation of sucrose was not markedly affected by the partial delamination of the electrodes shown in Figure 1.

Oxidation of Solcut BR Cutting Fluid

The tests with Solcut BR commenced after the rig had been commissioned with sucrose. The first run started with 2 g/l Solcut BR and the carbon mass balance was calculated at different stages during the run (Figure 3). The amount of carbon released plus the amount of TOC remaining in the electrolyte accounted for about 70 % of the measured TOC at the start of the run. There were some inconsistencies with the measurement of the COD and TOC around 500 hours. These were ascribed to the difficulties in taking representative samples, because the COD and TOC values varied in a similar manner. Despite the variations, it was concluded that the carbon mass balance confirmed that most of the Solcut BR had been oxidised to carbon dioxide.

The results were sufficiently encouraging to try a higher concentration of Solcut BR in the next run (8 g/litre instead of 2 g/litre) and a higher current (24 Amps instead of 12 Amps). It was noted that the Solcut BR emulsion was not stable during the oxidation: some oil droplets formed on the surface of electrolyte in the reservoir tank and in the tube housing the electrode. It was not possible to take representative samples for COD and TOC measurement, and so the effectiveness of the oxidation was judged solely by carbon dioxide generation. There was a “step effect” in the evolution of carbon dioxide. This occurred when the rig was shut down overnight and re-started the following morning (or after the weekend). It was presumed that this effect was due to separation of oil from the emulsion and its incomplete re-emulsification when the rig was re-started.

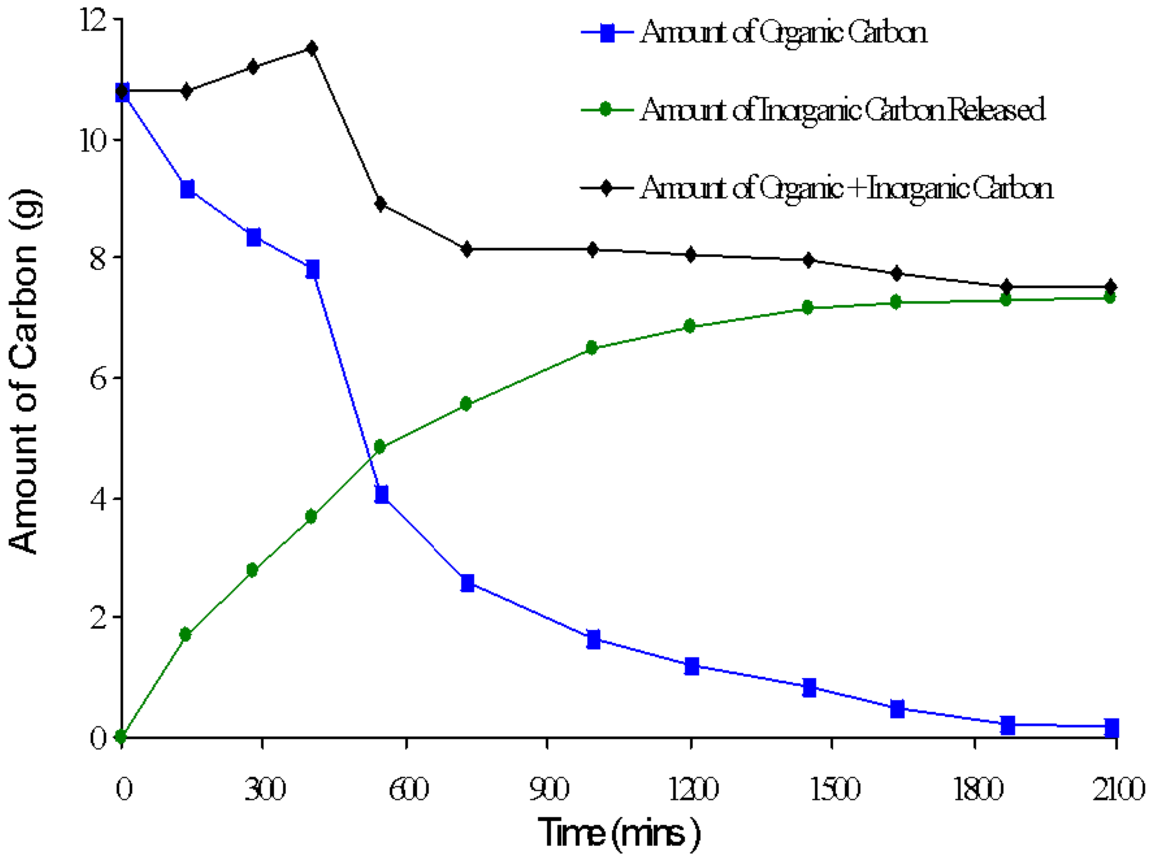

Fig. 3. Carbon mass balance for oxidation of Solcut BR

There were no discontinuities in carbon dioxide generation when the same concentration of Solcut BR was oxidised with the same current, but using continuous operation. There were differences in the pattern of carbon dioxide production between the 2 runs. Although the maximum concentration of carbon dioxide released into the purge gas was not affected, the peak of carbon dioxide generation was later and broader with continuous operation. Consequently, the total amount of carbon released as carbon dioxide was greater (40 g cf. 27 g). Continuous operation was seen to be beneficial and it was used for subsequent runs.

The next run examined the effect of doubling the initial concentration of Solcut BR to 16 g / litre. It was intended to also double the applied current to 48 Amps, but it was found that this caused the temperature of the electrolyte to rise to close to the maximum of 60 ^{o}C recommended by Condias. Accordingly, the current was held at 48 Amps for only the first 2 hours of the run; thereafter it was held at 36 Amps.

Using a current of 36 Amps led to an increase in the maximum rate of carbon dioxide production (Table II). This was about 50 % higher than that with 24 Amps, as expected.

Table II. Oxidation of Solcut BR

Set of Electrodes	First		Third		
Cumulative Usage at Start of Run (Amp.hours)	2,200	3,400	408	11,000	12,700
Run Time (hours)	53	75.47	42.5	25	23
Current (Amperes)	24	48 A for first 2hrs 36 A for remainder	24	24	24
Initial [Substrate] (grams/litre)	8	16	8	8	8
Initial Amount of Solcut BR (grams)	60	120	60	60	60
Max. Concentration of Generated CO_2 in Outlet Gas (% v/v)	0.59	1.0	0.67	0.34	0.16
Amount of Carbon Liberated as CO_2 (grams)	40	90	19.2 at 24 hrs 21.6 at 42.5 hrs	10.5	5.2

All continuous operation

The fact that the increase in carbon dioxide production was proportional to the increase in the current indicated that the higher concentration of cutting fluid was being oxidised efficiently. This conclusion was supported by the observation that the amount of carbon liberated as carbon dioxide increased approximately 2 fold from 40 g to 90 g in line with the increase in the added organic material.

The first set of electrodes retained their ability to oxidise Solcut BR for at least 3,400 Amp hours of operation (Table II). However, the third set of electrodes was not as active or as stable as the first set. When the third set was applied to the oxidation of Solcut BR after only 408 Amp. hours of previous operation, only 22 g of carbon was liberated from 60 g Solcut BR, whereas 40 g carbon had been liberated by the first set after 2,200 Amp.hours of previous operation (Table II). Moreover, the activity of the third set decreased with further usage. There was a decrease both in the maximum concentration of carbon dioxide generated and in the total amount liberated. This is illustrated in Table II by the amount of carbon released as carbon dioxide during the first day of operation. Batch operation was such that by 24 hours of operation the concentration of carbon dioxide in the outlet gas was only slightly above that present in the atmosphere.

Oxidation of Mineral Oils

After confirming that the electrodes could oxidise Solcut BR, work with the first set of electrodes moved on to the next stage, which was to examine the oxidation of the mineral oils. Two runs with mineral oils were performed (Table III). The first examined a hydraulic oil, OM 81, at 8g/l, which was mixed with a commercial “degreasing” detergent (Brillo) at 0.8 g / litre. Oxidation was performed with a current of 24 Amps. However, it was found that the concentration of carbon dioxide released into the outlet gas was never greater than about 0.04%, which was much less than that with 8 g/l Solcut BR (Table II).

An attempt was made to increase the rate of carbon dioxide production by the following sequence of actions:-

(i) removing the electrolyte and stirring it vigorously using an overhead mechanical stirrer before returning it to the rig,
(ii) adding an extra at 0.8 g / litre Brillo and stirring,
(iii) adding an extra 20 g $Na_2SO_4.10H_2O$ (i.e. 2.67 g / litre) to the electrolyte,
(iv) removing 3 litres of electrolyte, heating it to 90^oC, and then adding it back to the rig. This increased the temperature of the electrolyte to ~ 60 ^oC. It was hoped that the heating to 90^oC would stimulate oxidation by any persulphate present in the electrolyte.

None of these actions resulted in any marked increase in the rate of formation of carbon dioxide.

It was argued that the lack of oxidation could have been due to poor emulsification of the mineral oil, and so the work then focused on how to prepare emulsions of the mineral oils that were similar to Solcut BR emulsions. A range of commercial surfactants was examined, and a 1:1 mixture of Atlas G1096 and Brij 92V (supplied by Uniqema) was found to be effective with a range of oil types. When the emulsifiers were mixed into the oil, both at 10 % by weight, the mixture produced a fine, milky emulsion upon dilution in water. The appearance of the emulsion was similar to that with Solcut BR.

Table III. Oxidation of Mineral Oils

Set of Electrodes	First		Second	Third
Cumulative Usage at Start of Run (Amp.hours)	8,300	10,200	< 10	1,900
Run Time (hours)	78.25	68.7	54	27.3
Current (Amperes)	24	36	24	24
Initial [Substrate] (grams/litre)	8 g/l OM81 + 0.8 g/l Brillo	16 g/l OMD 80 [a] + 1.6 g Atlas G1096 + 1.6 g Brij 92V	16 g/l Tellus R10 + 1.6 g/l Atlas G1096 + 1.6 g/l Brij 92V	8 g/l Tellus R10 + 0.8 g/l Atlas G1096 + 0.8 g/l Brij 92V
Estimated Initial Amount of Organic Carbon [b] (grams)	51 g from OM81 + 0.3 g from Brillo	204 g from OMD 80 [a] + 16 g from Atlas G1096 + 5.3 g from Brij 92V	102 g from Tellus R10 + 8 g Atlas G1096 + 2.7 g Brij 92V	51 g from Tellus R10 + 4 g Atlas G1096 + 1.3 g Brij 92V
Max. Concentration of Generated CO_2 in Outlet Gas (% v/v)	0.04	0.18	0.11	0.06
Amount of Carbon Liberated as CO_2 (grams)	Not determined	5.2	16	1.8

[a] Volume of electrolyte = 15 litres
[b] Assuming composition of oil is $C_{17}H_{36}$

It was recognised that the addition of the surfactants would increase the amount of organics to be oxidised by about 10% (Table III). This was considered to be acceptable, if the emulsifiers proved to be successful.

Consequently, the next run tested a mixture of 16 g/l oil, 1.6 g/l Atlas G1096 and 1.6 g/l Brij 92V. OMD 80 was chosen as the mineral oil instead of OM 81, because it contains detergent additives. The emulsion was subjected to electrochemical oxidation at 36 Amps. Despite the presence of the emulsifiers, the amount of carbon released as carbon dioxide was still much lower than with Solcut BR (Table III cf. Table II). There was a slight increase in the concentration of carbon dioxide released into the outlet gas, which probably reflected the higher current (36 Amps vs. 24 Amps).

The 2 tests with the mineral oils indicated that the diamond-coated electrodes were unable to oxidise emulsified mineral oils. However, the tests had been conducted with electrodes that had lost a major part of their diamond coating. So it was not possible to determine whether delamination was the reason for the lack of oxidation, or whether emulsified mineral oils were intrinsically resistant to oxidation in this system.

A new set of electrodes was then examined with an emulsified mineral oil (albeit with a slightly different oil (Tellus R10)). However, oxidative performance was only slightly improved with these new electrodes (Table III). The total amount of carbon released as carbon dioxide was greater than with OM 81 and OMD80, but the maximum concentration of carbon dioxide in the outlet gas was lower. This second set of electrodes was observed to delaminate during the run. Nevertheless, some stimulation of carbon dioxide generation would have been expected if the new electrodes had been able to attack the oil emulsion (particularly considering that the maximum carbon dioxide production from Solcut BR was established in the early stages of a run.

The resistance of the emulsified mineral oils to oxidation was confirmed with the third set of electrodes using Tellus R10, also emulsified (at 8 g/l) with 0.8 g/l Atlas G1093 and 0.8 g/l Brij 92V surfactants). As before, the rate of oxidation and the amount of carbon liberated as carbon dioxide were very low (Table III). This was despite the fact that the initial emulsion had a white, milky appearance, which indicated that the oil was well emulsified.

The poor oxidation of the emulsified mineral oil was interpreted using the understanding of current efficiency and reaction kinetics gained from the runs with sucrose. In general, the rate of diffusion of a particle decreases as its size increases. With an emulsified oil the particle size of an emulsion droplet will be much greater than the size of a sucrose molecule. Thus, it was postulated that the slow rate of oxidation of the emulsified oils, even at the start of the reaction, could have been due to diffusion limitation. However, the same limitation should have applied to the oxidation of Solcut BR. Thus, the lack of oxidation of the mineral oils may be the result of other factors. Undoubtedly the instability of the diamond coating was a main factor, but it was thought possible that there may be others.

For example, there may be some property of the mineral oils that inhibited oxidation. This hypothesis was tested by adding sucrose to the electrolyte containing the emulsified Tellus R10. Two separate additions of 60 g sucrose were made. These led to an increase in carbon dioxide production. A further 17 g carbon was released as carbon dioxide after the first addition of sucrose, and 15 g after the second. But it was noted that the amount of carbon released was less than the amount of carbon produced with sucrose alone (Figure 4).

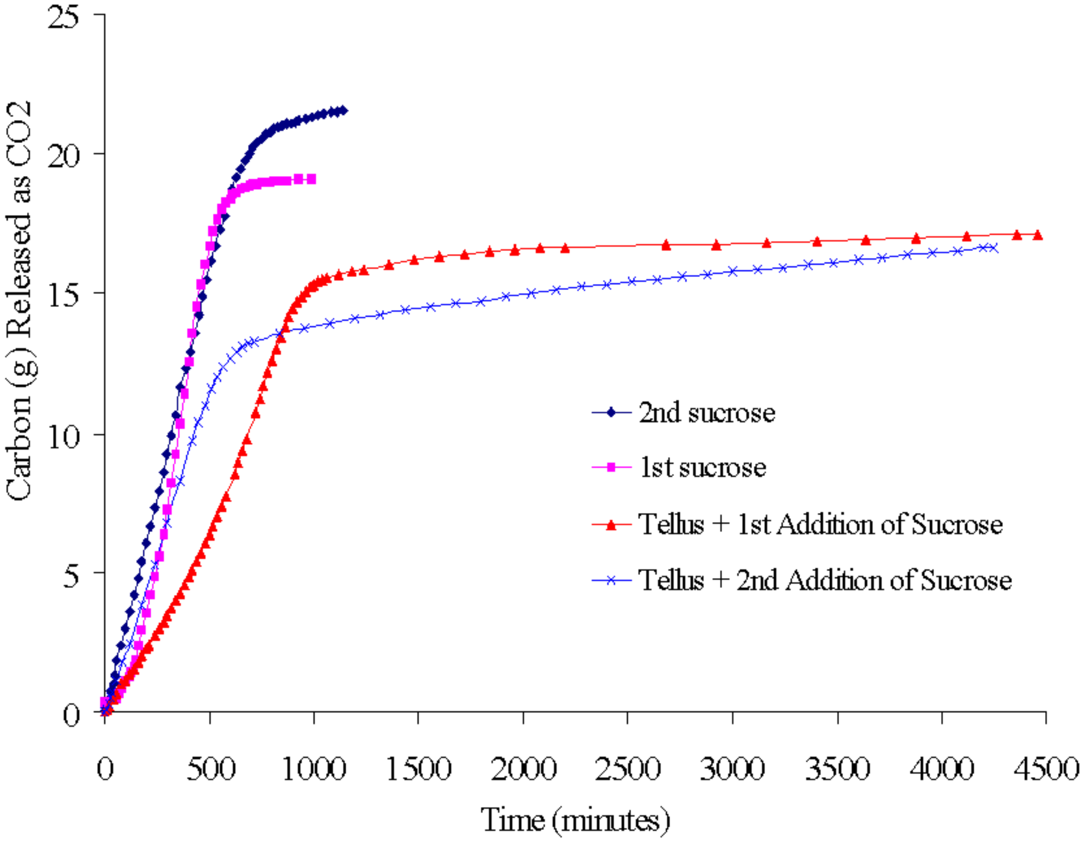

Fig. 4. Sucrose oxidation with and without emulsified Tellus R10

Furthermore, the initial rate of carbon dioxide production after the first addition was lower than the rates with sucrose alone. This indicated that there could indeed be some property of the emulsified mineral oil that inhibits the electro-oxidation of its organic components. The mechanism of the inhibition is not known.

CONCLUSIONS

The tests at AWE confirmed that an aqueous emulsion of Solcut BR cutting fluid can be oxidised to carbon dioxide electrochemically by using electrodes coated with boron-doped diamond. However, the work did not lead to a process to treat mineral oils. The reason for the inability to oxidise the mineral oils is not known. There are several possibilities, including:
(i) the loss of the diamond coating,
(ii) ineffective contact between the oil and the electrode surface,
(iii) some property of the emulsified mineral oil that inhibits or resists electro-oxidation.

The development of electro-oxidation with diamond electrodes for the treatment of oily waste will require not only a greater chemical understanding but also a supply of stable electrodes. Although the partially delaminated electrodes were able to oxidise sucrose, the results indicate that the oxidation of mineral oils will require pristine electrodes. The factors influencing electrode stability are being investigated [6], and electrodes prepared by alternative techniques are becoming available [7]. Thus, this technology still retains its potential for radioactive waste treatment.

REFERENCES

1 G.T. Taylor and V Freestone, “Experience of Biodegradation for the Disposal of Waste Machine Tool Cutting Fluid,” Proceedings of Waste Management ‘01 Symposium, Tucson, February 26 – March 1, 2001.

2 G.M. Swain, A.B. Anderson and J.C. Angus, “Applications of Diamond Thin Films in Electrochemistry”, MRS Bulletin, **23** (September), 56 - 60, 1998.

3 M. Fryda, T. Matthee, S. Mulcahey, M. Hofer, L. Schafer and I.Troster, “Applications of DIACHEM Electrodes in Electrolytic Water Treatment,” The Electrochemical Society *Interface,* Spring, 40 – 44, 2003.

4 C.J. Bates, G.T. Taylor, T. Matthee, M. Fryda and M. Stadelmann, “Evaluation of Electrochemical Destruction Using Diamond-Coated Electrodes for the Treatment of Waste Lubricants,” Proceedings of Waste Management ‘03 Symposium, Tucson, February 24 - 27, 2003.

5 Michaud P-A
Comportement Anodique du Diamant Synthetique Dope au Bore, PhD These No. 2595, Ecole Polytechnique Federale de Lausanne, 2002.

6 L. Schafer, S. Arndt, D. Herrman, M. Hofer, D. Becker and K. Juttner, “ Diamond Electrodes Under High Current Density”, 7th Workshop DIAMOND ELECTRODES, October 18 – 20, 2004 Interlaken, Switzerland.

7 W. Wesner and G Nauer, “Industrial Production of HTHP-BDD Electrodes and their Applications in Wastewater Treatment”, 7th Workshop DIAMOND ELECTRODES, October 18 – 20, 2004 Interlaken, Switzerland.