

Demonstration Of Electrochemical Oxidation Of Oils Using Boron-Doped Diamond Electrodes And Its Potential Role In The Disposal Of Radioactively Contaminated Waste Lubricants - 9035

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

C.R. King, K. Dawes, Windsor Scientific Ltd., 264 Argyll Avenue, Slough, SL1 4HE, UK.

ABSTRACT

Electrochemical oxidation using a boron-doped diamond (BDD) anode is being investigated as a possible method for treating radiologically-contaminated oils. It has the potential to oxidise oils to carbon dioxide and water, and it would be particularly beneficial for oils contaminated with plutonium. It was found that simultaneous application of sonication and electro-oxidation produced and maintained an oil emulsion, so enabling its oxidation. This treatment was shown to be effective with 3 different oils: an unused hydraulic oil, an unused vacuum pump oil and a waste used machine tool oil, although the addition of a small amount of surfactant was required for the effective emulsification and oxidation of the vacuum pump oil. Essentially complete oxidation of the hydraulic oil in the absence of other organic material was demonstrated.

The rate of oxidation appeared to be limited by the applied current when the concentration of oil was high and the current was low. Similarly, it was limited by the oil concentration when the concentration of oil was low and the current was relatively high. The required scale-up from a laboratory electrochemical cell is estimated to be 10,000 fold, which could entail a cell with a total BDD surface area of 3m², drawing a current of about 2000 A. It is anticipated that it should be possible to minimise the size of the cell by optimisation during the design of the prototype equipment.

INTRODUCTION

The disposal of waste radiologically-contaminated oils has been and remains problematic in the UK. Oils are not compatible with the aqueous waste treatment processes at AWE (formerly known as the Atomic Weapons Research Establishment), and the potential to immobilise oils for disposal as solid waste to the UK's Low Level Radioactive Waste repository is limited [1].

Some nuclear power plants in the UK incinerate oily wastes [2]. These plants were installed to treat wastes containing primarily beta and gamma emitting radionuclides rather than alpha radionuclides, and they are not available to AWE. However, since 2004 AWE has been able to dispose of oils containing very low levels of radioactivity at a commercial incinerator [3]. This route cannot be used for AWE's entire legacy of oily wastes because the incinerator's discharge consent for alpha activity is limited to 60 MBq per annum from all sources.

AWE subsequently identified a very promising option for the treatment of oils contaminated with uranium. The treatment, which involves extracting the oil with sulphuric acid, was developed by the former BNFL Research and Technology group (now the UK National Nuclear Laboratory) at the Springfields site for the fabrication of nuclear fuel. The benefit of this treatment is that the extracted uranium can be processed for incorporation into nuclear fuel. Trials with samples of AWE's uranium-contaminated oils demonstrated that it is possible, by repeated acid extraction, to decontaminate the oils sufficiently to enable them to be disposed of by controlled exempt release. Accordingly, AWE has

received authorisation to send uranium-contaminated oils to Springfields for recovery of the metal and disposal of the decontaminated oil [4].

The uranium-contaminated oils are the major contributors to both the legacy and the anticipated future arisings of oily wastes at AWE. Although the acid extraction process has the potential to deal with the bulk of the oily wastes, it will probably be unsuitable for the residual legacy of plutonium-contaminated oils. The application of acid washing to plutonium-contaminated oils is outside the operating license of the Springfields site. Moreover, it is likely that the decontamination factor would not be sufficient to make the treated oils suitable for controlled exempt release, because the specific activity of plutonium is at least 10^4 fold higher than the specific activity of uranium.

It was considered that the plutonium-contaminated oils will have to be destroyed to enable the plutonium to be conditioned for disposal. Electrochemical oxidation has the potential to oxidise the oils to carbon dioxide and water. The investigation of electrochemical oxidation has focused on the use of boron-doped diamond (BDD) electrodes [5,6,7] because of the benefits compared to other electro-oxidation processes, i.e.:-

- (i) the use of an electrolyte containing non-aggressive and non-corrosive chemicals,
- (ii) ease of disposal of the spent electrolyte,
- (iii) simple electrochemical cell configuration.

The investigation started with electrodes coated with a thin layer of BDD [5, 6], and then it moved on to study electrodes prepared from a single BDD wafer [7]. Although it was shown that a cutting oil could be oxidised, it was difficult to determine whether BDD was able to oxidise mineral oils, such as lubricating oils. Several methods to enhance oil oxidation were examined and eventually it was found that a system coupling sonication and electro-oxidation gave demonstrable oil oxidation. This paper outlines the investigation, and it discusses briefly some of the factors that would influence the development of a full-scale process.

EQUIPMENT, MATERIALS AND METHODS

Sonicator

The ultrasonic power was provided by a Hielscher UP100H laboratory scale ultrasonic processor equipped with a titanium sonotrode (Type MSL2D, 10 mm diameter x about 80 mm length). The sonicator was operated continuously at full power (100 W).

Electrodes and Cell

The BDD electrodes (DIAFILM PE™) were supplied by Windsor Scientific Ltd. The BDD was in the form of discs, of approximately 0.5 mm thickness x 2 cm diameter, mounted in a plastic body. The BDD discs have proved to be very robust, although it has been necessary to re-secure them in the electrode housing from time to time.

The electrical power was provided by either an Autolab PGStat30 potentiostat / galvanostat (EcoChemie B.V.) or an Electroplating power supply (Power Station pe1050). The Autolab was equipped with PC control through proprietary General Purpose Electrochemical System software (as supplied by Windsor Scientific Ltd). Electro-oxidation was performed at 0.1 Amperes unless indicated otherwise in the text. The laboratory cell generally operated at cell potential of 5 – 15 Volts.

The experiments were performed in the cell described previously [7], which comprised a narrow form 250 ml beaker fitted with a rubber bung that held a BDD anode and a stainless steel cathode. The electrolyte (with an initial volume of about 150 ml) was mixed on a magnetic stirrer. For those experiments using

sonication, the sonication horn was passed through the rubber bung, and the beaker was placed inside a copper cooling ring connected to a water bath chiller circulator (Grant LTD 20G) held at 18 °C.

Electrolyte

The electrolyte contained oil and sodium sulphate (generally 10 g Na₂SO₄.10H₂O / litre) in demineralised water. The initial concentration of oil was 8 g/litre unless stated otherwise. Sodium hydroxide was added at the start of the test, and further additions of 2M sodium hydroxide were made as required to maintain an alkaline pH.

All chemicals were obtained from commercial laboratory suppliers, except for:-

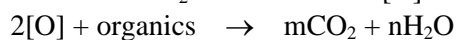
Shell Tellus Oil R10	Shell, UK Ltd., London
Edwards No 16 Vacuum Pump Oil	Edwards
Used oil	AWE - from a non radioactive machine tool
Atlas G-1096 non-ionic surfactant	Uniquema (formerly ICI Surfactants)
Brij 92V non-ionic surfactant	

Monitoring Oxidation

The oxidation was performed under alkaline conditions to trap the carbon dioxide as carbonate. The concentration of carbonate was measured by titration of 1ml or 0.5 ml samples against 0.02M hydrochloric acid using mixed indicators, viz. phenolphthalein followed by bromophenol blue when the phenolphthalein turned from pink to colourless [8]. The titre with bromophenol blue yielded the concentration of inorganic carbon (TIC) as bicarbonate. The titre with phenolphthalein yielded the concentration of hydroxide plus carbonate. Subtraction the second titre from the first gave the concentration of free hydroxide.

The measured values for the TIC of the samples taken during the oxidation runs were corrected for the dilution produced by the addition of alkali. The volumes of the samples taken and the volumes of added alkali were recorded and they were used to calculate a nominal change in the volume of the electrolyte. It was recognised that the volume of electrolyte would tend to decrease due to evaporation and electrolysis, and the resultant concentration factor was estimated from the acid/base titration (see above). Any increase in the total acid titre that was not linked to the addition of alkali was ascribed to evaporation / electrolysis of the electrolyte. The TIC values shown here have been normalised in this way to refer to the conditions at the start of the test.

The current efficiency of the oxidation was calculated on the basis of the reactions shown below.



It was assumed that the mineral oils have the nominal formula C₁₇H₃₆ so that oxidation proceeded according to the equation:-



The oxidation of 240 grams oil would yield 204 grams of carbon in 17 moles (748 grams) carbon dioxide. If this reaction occurs with 100% current efficiency, it would require the transfer of 52 x 2 moles of electrons (104 Faradays, which equals the charge delivered by 104 x 96479 amp.sec). Thus 0.1 A would produce 17 x 0.1 x 3600 / (104 x 96479) = 6.1 x 10⁻⁴ moles of CO₂ / hr = 7.3 mg inorganic carbon / hr.

RESULTS

The experiments on the oxidation of mineral oils have used mainly a lubricating oil for hydraulic systems, Shell Tellus Oil R10. Although any full-scale process would be operated under neutral to acidic conditions to allow the generated carbon dioxide to be removed in the off-gas, the laboratory tests were performed under alkaline conditions. This was done to enable the degree of oxidation to be monitored by the amount of inorganic carbon (TIC) trapped as carbonate in the electrolyte.

The results of a typical test with a BDD disc electrode are shown in Figure 1. The electrolyte contained Tellus R10 (at an initial concentration of 8g/litre) emulsified with 2 non-ionic surfactants (Atlas G1096 and Brij 92V) each at 0.8 g/litre. At the start of the run, there was a rapid rate of oxidation (i.e. TIC accumulation), but the rate of oxidation decreased after about 90 hours. The initial electrolyte was a uniform, optically dense emulsion without free oil, but during the run the emulsion thinned and free oil appeared on the surface of the electrolyte. It was concluded that the BDD anode had oxidised the surfactants causing the oil to separate from the electrolyte, so curtailing its further oxidation.

A test was performed with the emulsifiers but without oil. This produced less TIC over the same time (Figure 1) than the test with the emulsified oil, which showed that a small proportion of the emulsified oil had been oxidised along with the surfactants. Comparison of the TIC produced with and without the oil indicated that oil oxidation had generated about 1900 mg TIC /litre after 165 hours. However, this was equivalent to only about 30% of the added oil (see Methods section for the basis of the estimation).

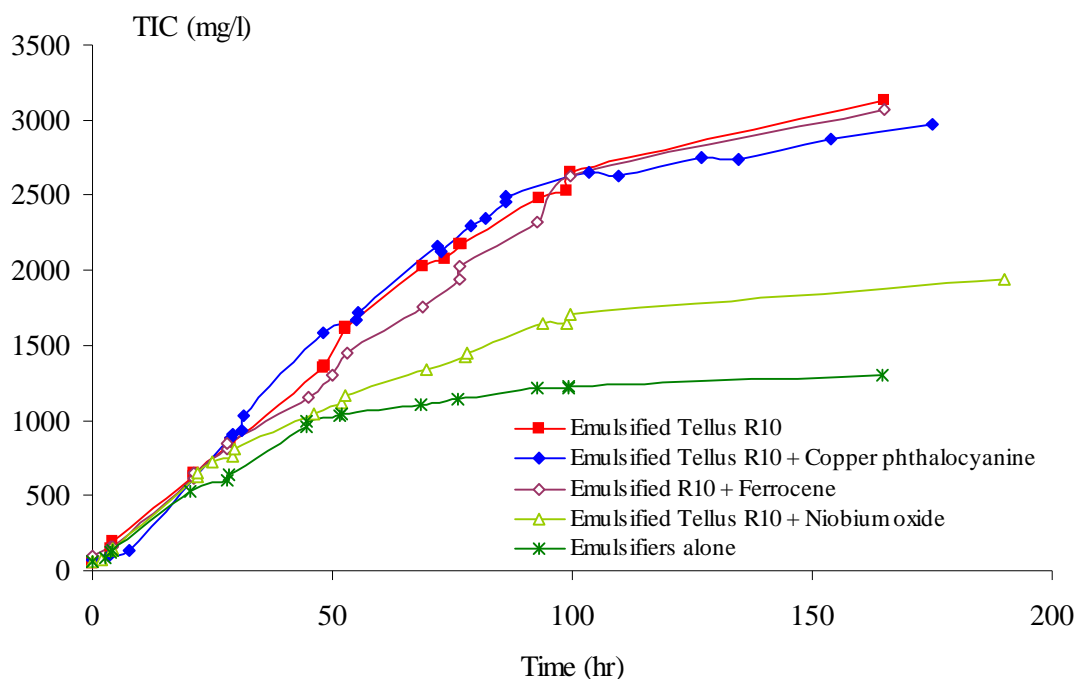


Fig. 1. Electro-Oxidation of Emulsified Tellus R10 Mineral Oil

Various attempts were made to stimulate oil oxidation by adding transition metal compounds that might act as redox couples (Figure 1). Copper and iron were added as oil-soluble compounds, copper phthalocyanine and ferrocene respectively, to the Tellus R10 to provide a concentration of 1g/litre metal in the oil (9 mg metal /litre of electrolyte). Niobium oxide, which is insoluble in water, was added as a fine powder directly to the electrolyte to yield a suspension of 700 mg metal /litre of electrolyte. These additions did not stimulate the oxidation of Tellus R10 emulsified with the Atlas and Brij non-ionic surfactants, and the presence of the suspension of niobium oxide was found to be inhibitory.

Sonication was then examined as a way to stabilise the oil emulsion during electro-oxidation. It was thought that it might overcome the apparent destruction of the surfactants. The simultaneous application of sonication and electro-oxidation was found to prolong the oxidation of Tellus R10 (Figure 2). Sonication and electro-oxidation was equally effective with 2 different oils: unused Edwards No 16 vacuum pump oil and a sample of waste oil taken from an old machine tool that was due for disposal at AWE (Figure 2).

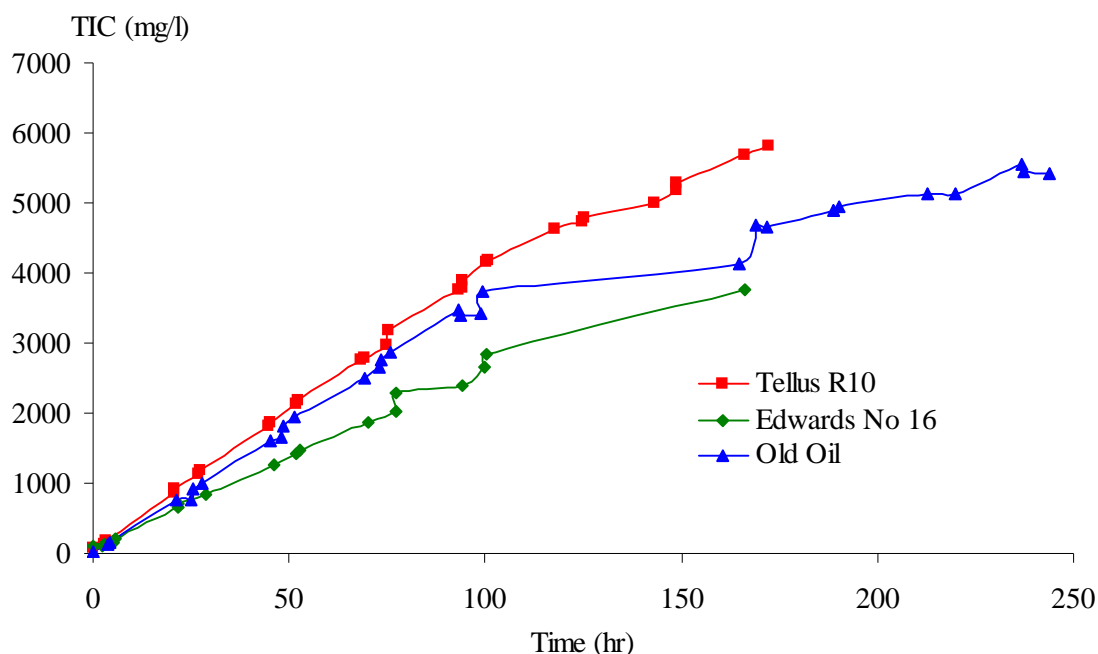


Fig. 2. Destruction of Emulsified Oil By Electro-oxidation Coupled to Sonication

The oxidation of the surfactants used to emulsify the oils represented a wasteful consumption of electricity. So the next set of tests examined whether the surfactants were still required when sonication was applied. An electrolyte containing Tellus R10 without any surfactant was sonicated for about 30 minutes before the start of electro-oxidation. The sonication produced a uniform, optically dense emulsion. The omission of the surfactants from the tests did not prevent the oxidation of Tellus R10 (Figure 3). The waste oil from the old machine tool behaved similarly to the Tellus R10. However, it was found that sonication did not completely emulsify a vacuum pump oil (Edwards No16) in the absence of surfactants. The addition of 2 drops of the oil soluble surfactant (Brij 92 V) after about 18 hours produced a uniform emulsion, which then initiated the oxidation of Edwards No16. It was estimated that the amount of surfactant added was about 0.3 g/litre, which was less than the amount used in the tests shown in Figures 1 and 2.

Conceivably the accumulation of TIC in the alkaline electrolyte could have been due to the absorption of carbon dioxide from the atmosphere. Accordingly, a control test was performed under alkaline conditions, but with no applied current. The electrolyte was prepared with oil and alkali, and further alkali was added during the run to produce a high pH similar to the pH values encountered briefly during the other runs. The control conditions did not lead to an appreciable absorption of carbon dioxide (Figure 3), and it was concluded that the formation of inorganic carbon was due to oxidation of the oils.

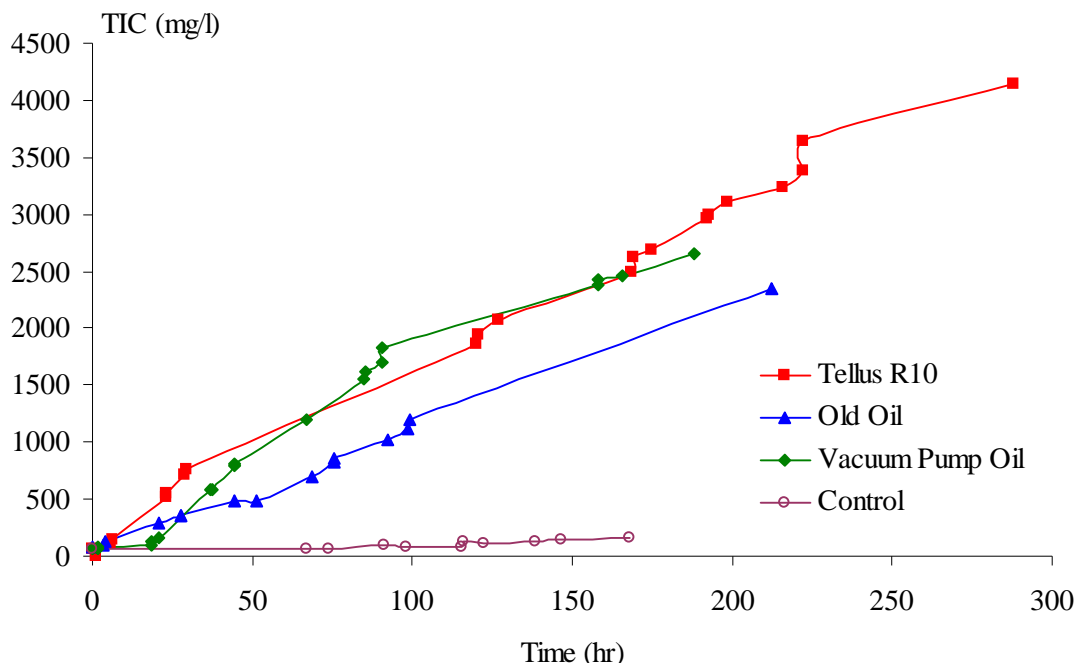


Fig. 3. Destruction of Oils in the Absence of Surfactants by Electro-oxidation Coupled to Sonication

This was the first demonstration that electro-oxidation with a BDD anode is able to destroy mineral oils in a simple chemical system. However, the tests did not demonstrate complete oxidation. In the test shown in Figure 3 the oxidation of 8g/l Tellus R10 produced 4500 mg TIC / litre after nearly 300 hours, equivalent to 66% destruction. Subsequently, complete oxidation was demonstrated by reducing the initial concentration of Tellus R10 from 8g/litre to 2g /litre whilst maintaining the current at 0.1 A (Figure 4). In this test, the concentration of TIC after 167 hours was 1700 mg /litre, which was the same as the nominal concentration of organic carbon at the start of the test.

However, the oxidation of 2g/litre Tellus R10 was achieved at a lower overall rate. When starting with 2g/litre Tellus R10, the maximum rate of formation of TIC was 1.9 mg carbon / hour, compared to 3.1 mg carbon / hour when starting with 8 g/litre Tellus R10. These values correspond to current efficiencies of approximately 26 % and 43% respectively (see the Methods section).

The maximum rates of oxidation were achieved at the start of the oxidation runs (Figure 4). It was considered that an understanding of the factors affecting the rate and extent of oxidation would have an impact on the further development of this process. Any improvement in the overall current efficiency of the oxidation would reduce the size of any future plant and reduce its consumption of electrical energy.

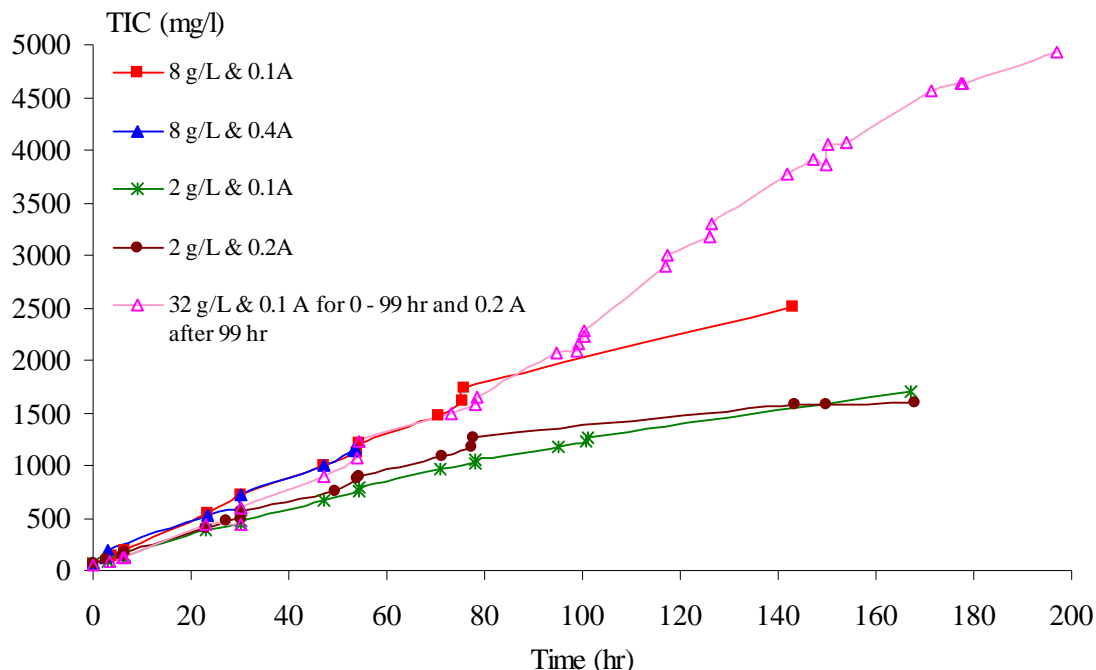


Fig. 4. Effect of Oil Concentration and Current on Rate of Oxidation of Tellus R10

It was possible to increase the rate of oxidation of Tellus R10 by increasing both the oil concentration and the applied current (Figure 4). A test was started with 32g/litre Tellus R10 and 0.1 A, and after 99 hours, the current was increased from 0.1 to 0.2 A. The increase in the current produced an immediate increase in the rate of formation of TIC from about $2.6 \text{ mg TIC}\cdot\text{hour}^{-1}$ at 0.1 A to about $6.2 \text{ mg TIC}\cdot\text{hour}^{-1}$ at 0.2 A.

The rate of oxidation of a water soluble compound is generally limited by the concentration of the compound when the cell is operated at a high current, and conversely, it is limited by the applied current when the cell is operated with a high concentration of oxidisable compound [6,9]. With the tests shown in Figure 4, the rate of formation of TIC with 32g/litre Tellus R10 was approximately proportional to the current, which implied that the rate of oxidation of the oils under these conditions was limited by the current.

On the other hand, the oxidation of 2g/litre Tellus R10 appeared to be concentration limited, because doubling the current (from 0.2 A to 0.1 A) had no appreciable effect on the rate of oxidation (Figure 4). If the rate of oxidation had been current limited, it would have increased by 2 fold. This conclusion was confirmed by examining the effect of the applied current on the rate of oxidation of 8g/litre Tellus R10 (Figure 4). The test used 0.4 A so that the ratio of initial oil concentration to current was the same as with 2g/litre Tellus R10 and 0.1 A. The electrical resistance of the electrolyte had to be reduced in order to apply the higher current. This was achieved by increasing the concentration of sulphate by about 5 fold. Again, the application of a higher current did not lead to a greater rate of oxidation (Figure 4). This result implied that the oxidation of 8g/litre Tellus R10 with either 0.1A or 0.4 A was also limited by the initial oil concentration.

However, this interpretation may be too simplistic, because the response of the rate of oxidation to the change in oil concentration was not as expected. The 4 fold reduction in the oil concentration from 8g/litre to 2g/litre did not produce a 4 fold reduction in the maximum rate of oxidation. Furthermore, operation at current limitation usually leads to maximum current efficiency, but the oxidation of 32 g/litre Tellus R10, which appeared to be current limited, did not occur with 100% current efficiency, the actual

current efficiencies being 35% and 42% at 0.1 and 0.2 A respectively. The theory of current/concentration limitation as applied to the oxidation of water soluble compounds may not be directly applicable to an oil emulsion, where the variables of the size and number of oil droplets are probably more important than the overall oil concentration.

DISCUSSION

The experiments outlined in this paper have demonstrated that, in principle, electro-oxidation with a BDD anode is capable of destroying oils. Further development will be required to scale-up this technology if it is to be used to condition waste, radiologically contaminated oils. Operation of the laboratory apparatus with 32 g/litre Tellus R10 and 0.2 A (Figure 4) produced a maximum rate of oxidation of 1 g oil/week, whereas a rate of oxidation of 10 kg / week may be a realistic target. Thus, the performance of the laboratory apparatus will probably have to be scaled-up by about 10,000 fold.

Scaling-up by 10,000 fold would entail a current of about 2000 A. However, the required proportional increase in the rate of oxidation with the increase in current will only be achieved if the rate of oxidation is limited by the current rather than by the concentration of the oil. The oxidation reactions with boron-doped diamond are thought to occur in a reactive zone that is at or very close to the surface of the anode [9], so it should be possible to avoid concentration limitation by improving the contact between the oil and the BDD anode, e.g. by increasing the surface area of the BDD anode. The existing electro-oxidation cell, which incorporates an electrode with a surface area of 3cm², could be operated at 0.2 A under current limited conditions provided that the concentration of oil was 32 g/litre. Scaling this up to accommodate 2000 A would require an electrode area of 30,000 cm², i.e. 3 m². It is likely that any full-scale plant would be assembled from modules, e.g. from 10 cells each holding 0.3 m² of BDD and drawing 200 A.

Oil would have to be fed into the full-scale plant during operation in order to maintain current-limitation. This could be done semi-continuously by periodic addition of oil provided that the minimum effective concentration is maintained. When all the oil had been added, the current could be gradually reduced as the concentration of oil in the electrolyte decreases.

The electrochemical cell would require a considerable amount of electrical energy for electro-oxidation, sonication and cooling. It has been found that the laboratory cell can be operated at a cell potential of 5 – 10 V, so the electrical power required could be as much as 10 – 20 kW for electro-oxidation alone. On the laboratory scale, the sonication used more energy than the electro-oxidation, so that cooling of the electrochemical cell was necessary. However, it is anticipated that optimisation of the cell geometry should reduce the energy requirement. There should be scope to improve the current efficiency, reduce the cell potential and minimise the input of sonication energy, all of which will reduce the amount of cooling energy required. Moreover, it may prove to be chemically advantageous to operate a full-scale plant at a higher temperature.

CONCLUSION

It has been demonstrated that electro-oxidation with a BDD anode is capable of destroying different oils when it is coupled to sonication. This confirms its potential role for the treatment of waste oils and, by implication, for the treatment of other organic non-aqueous phase liquids. The process could be used at AWE to complement the existing disposal routes for radiologically contaminated oils, i.e.:-

- (i) incineration of very low activity oils at a commercial facility, and
- (ii) decontamination of uranium contaminated oils at the UK National Nuclear Laboratory's site at Springfields.

Electro-oxidation with BDD could be used to treat those oils, such as plutonium-contaminated oils, that are not compatible with off-site incineration or decontamination.

The application of electro-oxidation at AWE would require approximately a 10,000 fold scale-up from the laboratory electrochemical cell. This would entail a cell with a total BDD surface area of 3m^2 , drawing a current of about 2000 A, and requiring as much as 10 – 20 kW for electro-oxidation alone. It is anticipated that it should be possible to minimise the size of the cell by optimisation during the design of the prototype equipment.

REFERENCES

- 1 J. Evans, A. Dietzold and G. Halliwell “Conditions for Acceptance by LLW Repository Limited of Radioactive Waste for Disposal at the Low Level Waste Repository (CFA)”, LLW Repository Ltd., CFA 01/08, 01 April 2008.
- 2 R E Streatfield, “Contaminated Oil Management”, Nuclear Future, Volume 01, No.2, pages 82-85.
- 3 Environment Agency, “Radioactive Substances Act 1993, Certificate of Authorisation and Introductory Note, Disposal of Radioactive Waste From Nuclear Site, AWE plc”, Authorisation Number BR8441, effective date 1st September 2004, superseded by BZ1994, effective date 1st March 2007.
- 4 Environment Agency, “Radioactive Substances Act 1993, Variation Notice, AWE plc”, Authorisation Number BZ1994, Variation Notice Number CC7544, effective date 1st December 2008.
- 5 C.J. Bates, G.T. Taylor, T. Mathee, M. Fryda and M. Stadelmann, “Evaluation of Electrochemical Destruction Using Diamond-Coated Electrodes for the Treatment of Waste Lubricants”. Proceedings of WM’03 Symposium, (Tucson, February 24 - 27, 2003).
- 6 G.T. Taylor and A.W.E. Newey, “Development of Electrochemical Oxidation Using Diamond-Coated Electrodes for the Treatment of Waste Lubricants: Part 1 Assessment of Potential”. Proceedings of WM’05 Symposium, (Tucson, February 27 – March 3, 2005).
- 7 G.T. Taylor, I.A. Sullivan and A.W.E. Newey, “Assessment of Electrodes Prepared from Wafers of Boron-Doped Diamond for the Electrochemical Oxidation of Waste Lubricants”, Proceedings of Waste Management ‘06 Symposium, February 26 – March 2, 2006, Tucson, USA, WM Symposia Inc. (2006).
- 8 R. Belcher and A.J. Nutten. “Quantitative Inorganic Analysis”, 2nd Edition, Butterworths, London, page 187 (1960).
- 9 P-A. Michaud, “Comportement Anodique du Diamant Synthetique Dope au Bore”, PhD These No. 2595, Ecole Polytechnique Federale de Lausanne, 2002.