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# The Removal of Technetium from EARP Waste Streams, Phase III

AEA Technology

R&D Technical Report P55

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# The Removal of Technetium from EARP Waste Streams, Phase III

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Research Contractor:  
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R&D Technical Report P55



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This report summarises the findings of research using a commercially available flowcell to demonstrate the electrochemical reduction method for the removal of the pertechnetate anion from flowing solutions as insoluble technetium dioxide. The information in this report is for the use of Environment Agency Staff and others involved in developing abatement systems for the removal of technetium from radioactive liquid waste streams.

**Research contractor**

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# Executive Summary

EARP was conceived primarily to remove  $\alpha$  activity from Sellafield discharges. Discharges of  $\beta/\gamma$  radionuclides were also reduced where this could be reasonably achieved. The major species remaining in the permeate after treatment are  $^{99}\text{Tc}$ ,  $^{90}\text{Sr}$ ,  $^{106}\text{Ru}$  and  $^{137}\text{Cs}$ , with the technetium providing nearly 90% of the activity.

During the first phase of this programme direct electrochemical reduction of the pertechnetate anion to insoluble technetium dioxide was identified as a potential technique for the removal of the technetium.

In the second phase of the programme the interferences posed by other species such as Sr, Sb and Ru were investigated. It was found that in the presence of other oxidising agents (such as ruthenium), an induction period was observed prior to the technetium removal. The second phase also established that the technetium bearing coating slowly corroded; although, in the short term, this corrosion was prevented by the use of cathodic protection.

In this phase of the programme we have compared several cathode materials and have found that the best decontamination kinetics were provided by platinised titanium and carbon cathodes (decontamination factors of 35 were achieved using these materials compared to approximately 10 in the same period using various steel cathodes).

We have also confirmed that the cathodic protection route almost completely inhibited the release of technetium from an electrodeposit over a period in excess of 1000 hours.

By using a small piece of platinum wire as the cathode, we have determined that the maximum amount of technetium that could be deposited onto the electrode was approximately  $4.85 \times 10^{11}$  Bq per square metre of electrode. Under genuine conditions, this amount of activity would be present in  $2.4\text{m}^3$  of waste.

The Porocell was commissioned and operated with manganese in the form of permanganate as an inactive simulant for technetium. The cell was extremely effective at removing manganese from the solution, with decontamination from 300ppm Mn to less than 1ppm Mn being achieved. A batch loading experiment was performed in which the manganese removal rate was maintained at 50ppm to less than 1ppm Mn in four litres of liquor per hour (0.2g manganese per hour). The concentration of manganese remained below 1ppm (DF 50) for over 60 hours. The final loading of manganese  $84\text{mg}/\text{cm}^2$  of geometric electrode area.



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# 1. Introduction

## 1.1 BACKGROUND

The information presented in Figure 1 illustrates a typical composition of Medium Active Concentrate (MAC) feed to, and produced by the active pilot plant, used in the development work, for the Enhanced Actinide Removal Plant (EARP). It should however be noted that there are noticeable differences in compositions of various MAC tanks that are being treated in the EARP plant and that the values used may represent the maximum activities present.

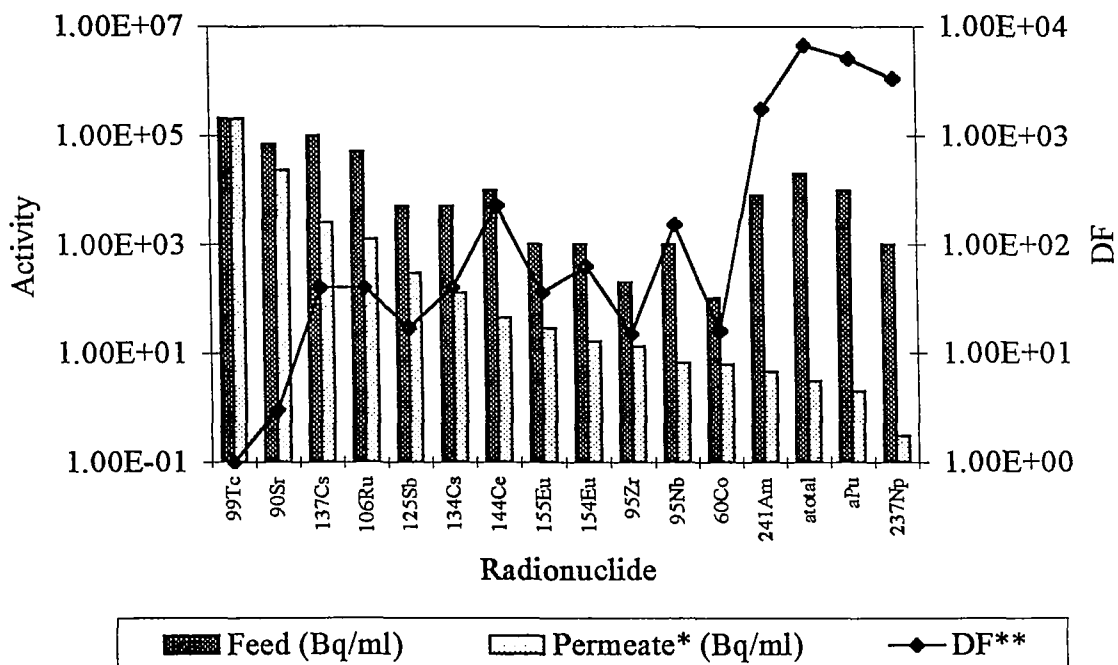


Figure 1 Variation in Feed activity, permeate activity and decontamination factor during EARP treatment of MA type stream.

EARP was conceived primarily to remove  $\alpha$  activity from Sellafield discharges and is now performing this task well. The opportunity was also taken to significantly reduce  $\beta/\gamma$  discharges where this could be reasonably achieved. These results, in terms of feed activity, permeate activity and decontamination factor, are illustrated in Figure 1. The major species remaining after treatment are <sup>99</sup>Tc, <sup>90</sup>Sr, <sup>106</sup>Ru and <sup>137</sup>Cs. In Figure 2 the activity of the radionuclides is expressed in terms of the total permeate activity.

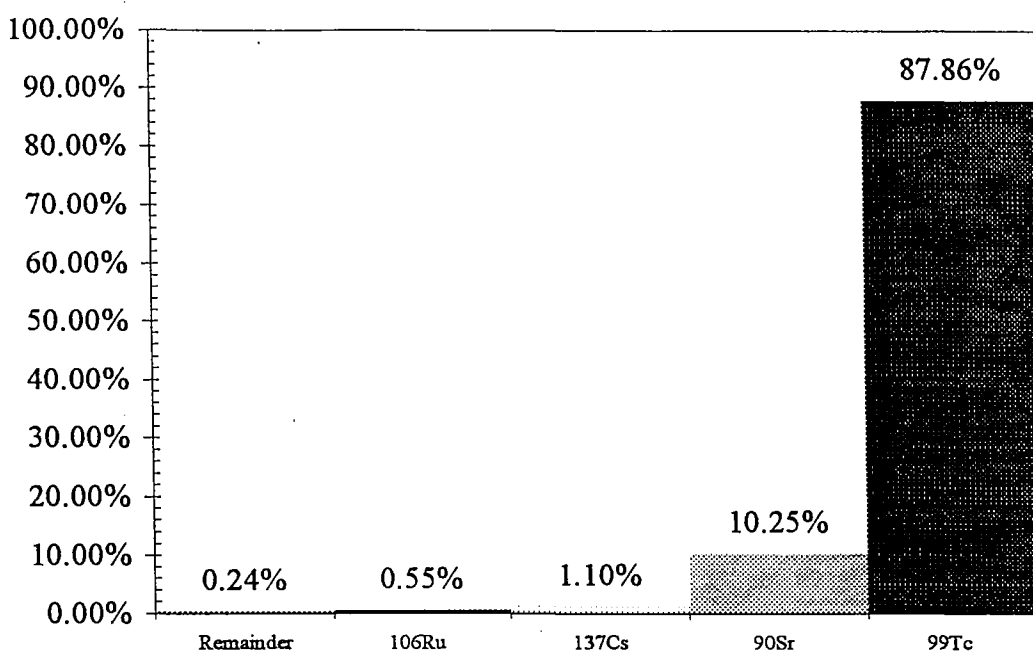


Figure 2 Activity content of liquor after EARP treatment of MA type stream.

From Figure 2, we can see that nearly 90% of the solution activity is present as technetium.

## 1.2 PREVIOUS RESULTS

During the first phase of this programme a number of techniques were compared for the removal of pertechnetate from an alkaline nitrate stream. Direct electrochemical reduction of the pertechnetate anion to insoluble technetium dioxide provided the best results of the methods examined (electrochemical ion exchange, seeded ultrafiltration, homogeneous reduction and electrochemical reduction).

The second phase of the programme was designed to investigate the electrochemical removal of technetium in the presence of other species (Sr, Sb and Ru). It was found that in the presence of other oxidising agents (such as ruthenium), an induction period was observed prior to the technetium removal. The second phase also established that the technetium bearing coating slowly corroded, although this corrosion was prevented by the use of cathodic protection. Treatment of genuine EARP permeates produced excellent results. Technetium DFs of greater than the target value of 10 were easily achieved (actual values 1700 and 650 were observed during sequential experiments).

## 1.3 PHASE III OBJECTIVES

The objectives of the phase were:

- (i) To take delivery of a "Porocell" type electrochemical unit from EA Technology, to commission and to test this cell that is compatible with disposal drum geometry.
- (ii) To confirm the validity of the redissolution measures tested in the previous phase.

- (iii) To establish the maximum loading capacity of the electrochemical system, given certain performance criteria.

The work was divided into active and inactive experiments. The active experiments included:

- (i) The identification of the best cathode material, based on technetium removal.
- (ii) Long term tests to evaluate the rate of corrosion of the technetium coating and the efficacy of cathodic protection.
- (iii) Small scale loading experiments to determine how the rate of technetium removal varies with coating thickness.

The inactive experiments utilised permanganate as an inactive simulant for pertechnetate. The experiments included:

- (i) An examination of the corrosion of the cathode material in the feed.
- (ii) Porocell commissioning and testing at various currents and species concentrations.
- (iii) Loading experiments to determine the maximum manganese loading of the unit.





## 2. Experimental Work

### 2.1 TECHNETIUM ANALYSIS.

Technetium analysis was performed by  $\beta/\gamma$  counting. Samples were taken and 0.5ml of the solution was placed onto the planchette. The liquid was evaporated by placing the planchette under an infra red lamp. The equipment used was an LND Pancake  $\alpha/\beta/\gamma$  Detector (7311/8767) combined with a Harwell 6000 series 6255 scalar timer unit. In order to examine the effect of salt shielding of the  $\beta$  particles, samples were prepared with a fixed technetium content of approximately 11Bq, and varying salt content (0, 20, 40 and 60% of the 260g/l sodium nitrate). The variation of counts taken over a ten minute period with salt content is shown in Figure 3. The figure also provides the standard deviation of five repeat samples as a percentage of the total count. We can see that even a 20% salt loading results in a fifty percent reduction in the count rate. The other point that was striking was that at 60% salt loading, the analysis became unreliable since the standard deviation of the analyses (even after five repeats) was 5% of the mean count. Under these conditions, it would be difficult to analyse for DFs of 10 (the target value) with any great confidence. It was decided to dilute all the samples by a factor of five prior to evaporation and analysis. A calibration plot of count rate versus technetium activity is provided in Figure 4, which illustrates a linear variation of count (over a 60 minute period) with technetium content over a DF range of 1 to 40.

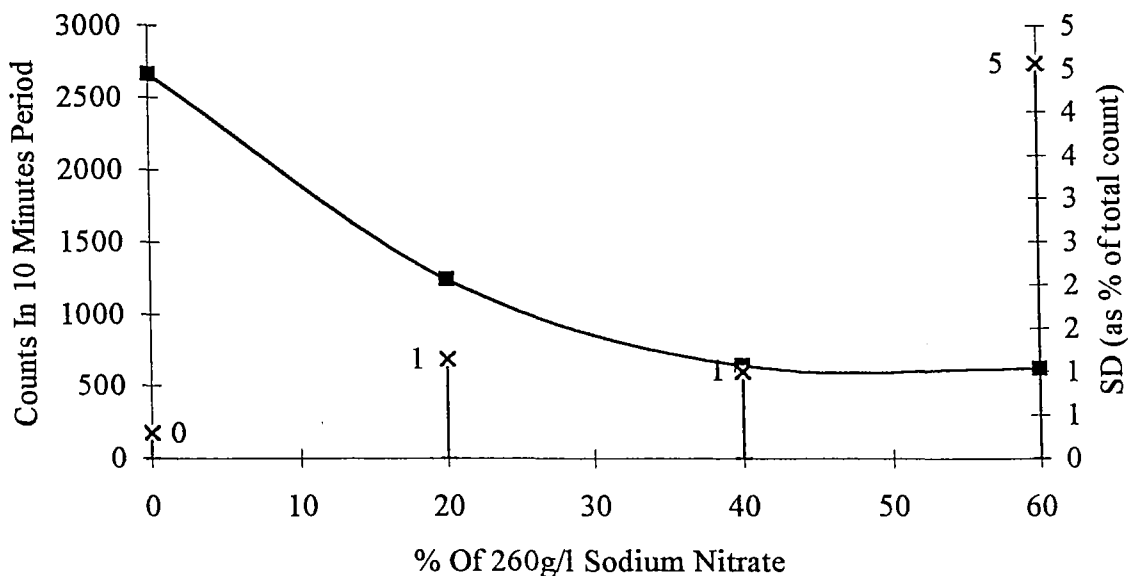


Figure 3 Variation Of Technetium Count With Salt Loading

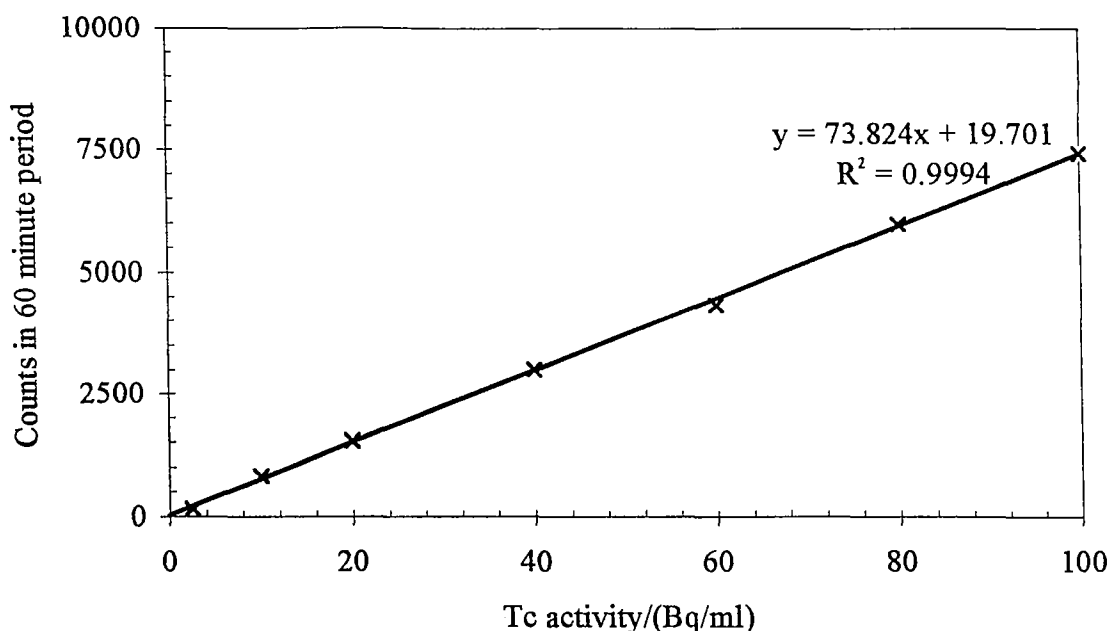


Figure 4 Variation Of Technetium Count Rate With Technetium Content

## 2.2 CATHODE CORROSION.

### 2.2.1 Aim

The proposed electroreduction process involves the production of a technetium deposit on the cathode. The production of other surface deposits, especially those formed by corrosion, may be deleterious to the system performance and also produce precipitates that would provide a route for the production of a secondary waste that would itself require either treatment or separation and storage. The aim of these experiments was to examine the corrosion behaviour of several electrodes under conditions pertinent to cell operation.

### 2.2.2 Method

The electrolyte for all the experiments was  $260\text{g/dm}^3$  sodium nitrate, with the pH adjusted to pH10.5 with sodium hydroxide. The working electrode geometric area was maintained at  $6(\pm 0.2)\text{cm}^2$  for all the experiments (Figure 5). The counter electrode was manufactured from platinised titanium. The reference electrode was a saturated calomel electrode (SCE). The solution was continuously stirred with a magnetic stirrer. The working electrode potential was set to -1V (versus SCE) and the variations of the cell currents with time were recorded.

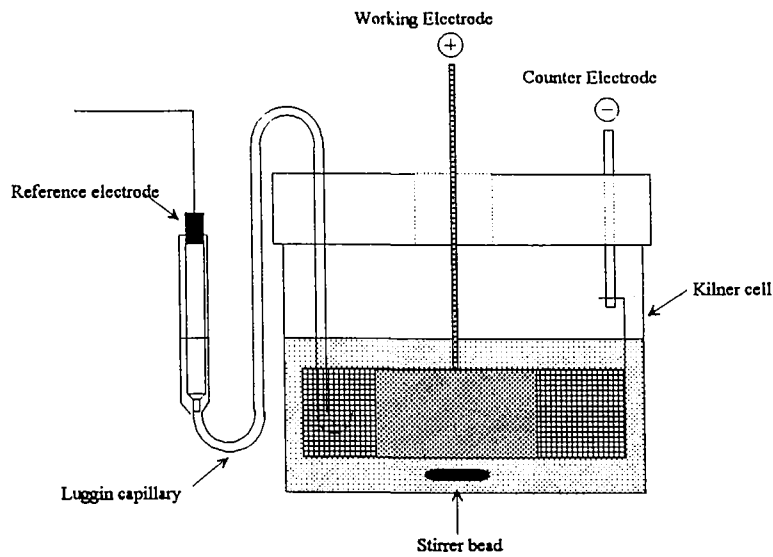


Figure 5 Kilner Batch Electrochemical Cell

It was also possible to observe any changes in the appearance of the working electrodes. The materials tested were mild steel, platinised titanium, type 304 stainless steel and type 316 stainless steel.

### 2.2.3 Results

The variation of cell current density with time is illustrated in Figure 6.

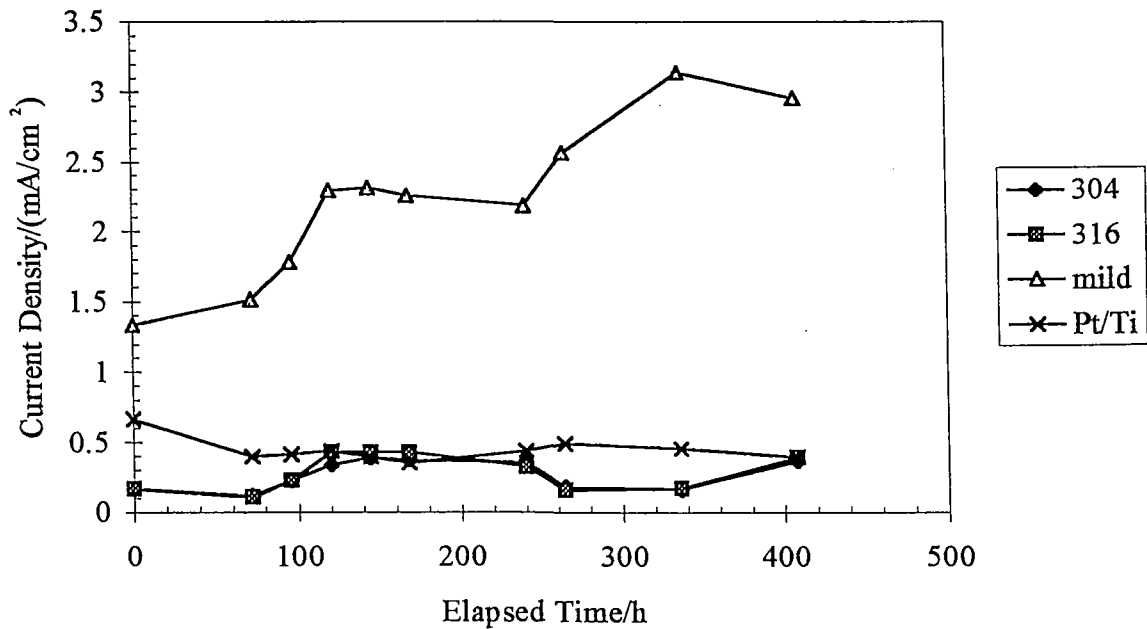


Figure 6 Variation Of Cell Current Density With Time During Corrosion Experiments

During the experiments, a small amount of a brown deposit was observed on the stainless steel electrodes, a large amount of a brown deposit was observed on the mild steel electrode and there was no visible deposit on the platinised titanium electrode. It was also noted that some of the deposit from the mild steel electrode had fallen off the surface and was suspended in the solution by the action of the magnetic stirrer.

From Figure 6 we can see that cell currents from both of the stainless steels were almost identical and remained low throughout the experiment ( $\approx 0.27(\pm 0.1)\text{mA/cm}^2$ ). The current density of the platinised titanium electrode gradually decreased over the first 100 hours and then stabilised at  $\approx 0.42(\pm 0.05)\text{mA/cm}^2$ . The current density of the mild steel electrode increased during the experiment from  $1.7\text{mA/cm}^2$  to  $3\text{mA/cm}^2$ .

#### **2.2.4 Conclusions**

The electrode current density results indicated that both of the stainless steel electrodes and the platinised titanium electrode were stable over the experimental period of 400 hours. The reduction currents observed with stainless steel electrodes were 35% less than the current recorded for the platinised titanium electrode. This indicates that the electrocatalytic activity of the platinised titanium electrode was higher, under the experimental conditions, than electrocatalytic activities of the stainless steel electrodes. The variation of current density with time for the mild steel electrode indicated a significant degree of instability.

The log of the visual observations indicated that the platinised titanium electrode was stable, stainless steel electrodes were slightly unstable and the mild steel exhibited a significant degree of instability.

The combination of the current/time data and visual observations indicate that the preferred electrode material, from a corrosion viewpoint, was platinised titanium. Both of the stainless steels would provide a reasonable alternative, whereas the mild steel would not be suitable since the rate of corrosion was too high with precipitates being noted in the stirred electrolyte.

### **2.3 TECHNETIUM REMOVAL KINETICS - VARIATION WITH CATHODE MATERIAL.**

#### **2.3.1 Aim**

In discussions with BNFL, we have identified that the main cost components of the electrodeposition technique are those involved with handling and storage. Thus the major cost savings are associated with minimising the number of cells required to perform the electrodeposition process. In this respect, the deposition kinetics are of primary importance. The aim of these experiments was to identify which electrode material provided the best electrodeposition performance.

### 2.3.2 Method

A batch cell of the type illustrated in Figure 5 was used for these experiments. For these experiments a more accurate simulant was produced by dissolving ferric nitrate, sodium dihydrogen phosphate and uranyl nitrate in 260g/dm<sup>3</sup> sodium nitrate to give a total volume of 250cm<sup>3</sup> and then adjusting the pH to 10.5 by addition of a suitable quantity of 3M sodium hydroxide prior to filtration through a 2µm polyamide filter. It was at this point that the technetium was added to the solution to provide an activity of 100Bq/cm<sup>3</sup>. The working electrode geometric area was maintained at 42(±1)cm<sup>2</sup> for these experiments. The counter electrode was manufactured from platinised titanium. The reference electrode was a saturated calomel electrode (SCE). The solution was continuously stirred with a magnetic stirrer. The working electrode potential was set to -1V (versus SCE) and samples of the electrolyte periodically taken for analysis by β/γ counting. The electrode materials tested included platinised titanium, 304 stainless steel, 316 stainless steel, mild steel and grafoil (a carbon composite sheet). The cell currents and voltages were recorded on a chart recorder.

### 2.3.3 Results

The variation of decontamination factor (DF), as defined in Equation 1, with time is illustrated in Figure 7.

$$\text{Equation 1 } DF = \frac{\text{Activity Of Feed Solution}}{\text{Activity Of Treated Solution}}$$

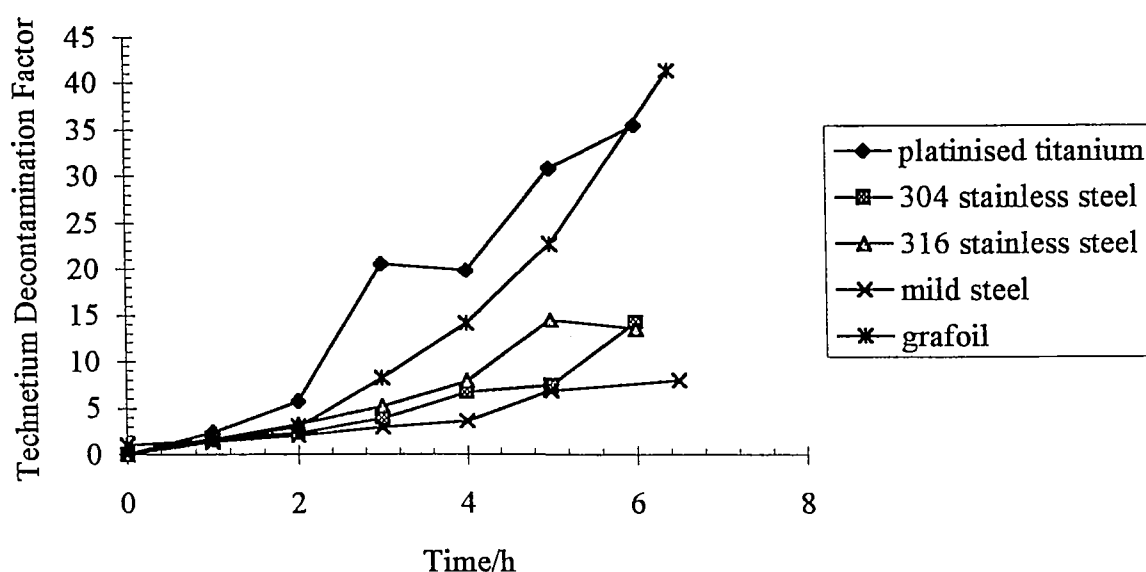


Figure 7 Variation Of Technetium DF With Time During Decontamination Experiments.

An approximate performance ranking of the materials (least effective first):

mild (8) < 316 stainless (13.5)  $\approx$  304 stainless (14.3) < platinised titanium (35.5)  $\approx$  grafoil (36.1)

The values in parentheses are the DFs attained after six hours.

The variation of current density with time for the five electrode materials is shown in Figure 8.

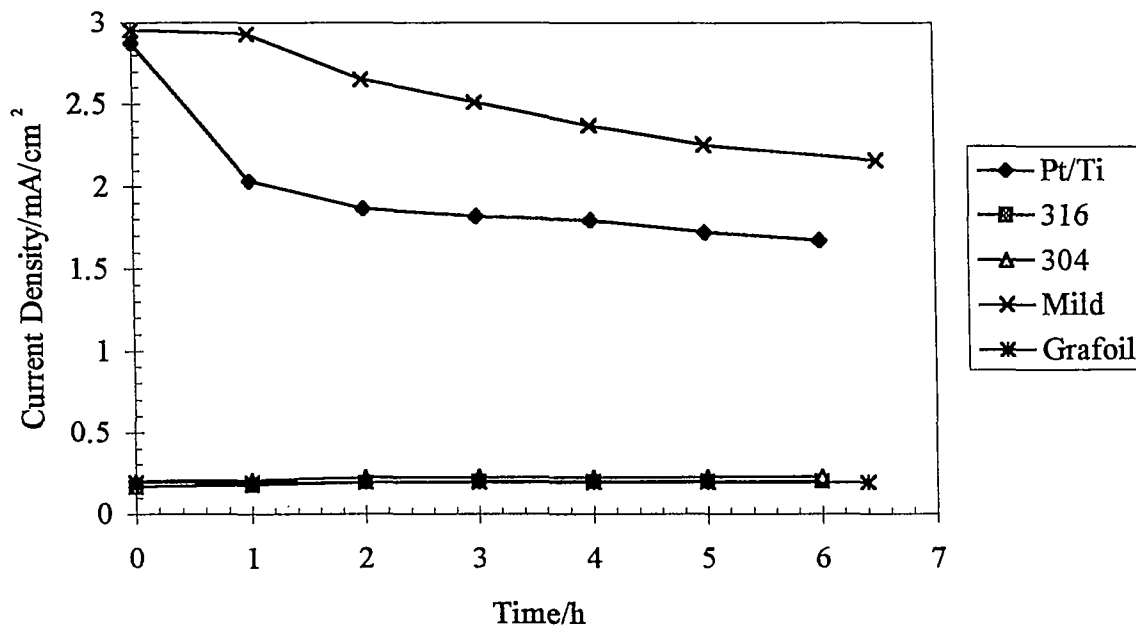


Figure 8 Variation Of Cell Current Density With Time During Decontamination Experiments.

From these results, the electrodes can be divided into two groups - those with high cell currents (platinised titanium and mild steel) and those with low cell currents (both stainless steels and the carbon grafoil). The variation in cell current between the two groups was almost an order of magnitude.

### 2.3.4 Conclusions

The objective of these experiments was to determine whether the variation of cathode material provided a route for enhanced performance by maximising the electroreduction kinetics. We have seen that the steel cathodes all provide adequate performance with DFs after 6 hours in the range of 8 - 14. The best treatment performance was provided by the platinised titanium and grafoil electrodes, with DFs after six hours treatment of approximately 36.

The current density results provided an indication of the power consumption that would be expected during operation. Once again, the electrodes were divided into two groups; the stainless steels and carbon gave low cell currents whereas the platinised titanium and mild steel both gave high cell currents. From the corrosion experiments in section 0, we can conclude that the high current observed when using platinised titanium was almost exclusively associated

with the reduction of solution species (nitrate and perhaps also the solvent) whereas the current observed with the mild steel was not only associated with solution electrochemistry, but also with solid state reactions such as corrosion. The stainless steels and carbon would appear to exhibit very little solid state electroactivity and low solvent and nitrate electrocatalytic activity.

## **2.4 CORROSION OF ELECTRODEPOSITED TECHNETIUM.**

### **2.4.1 Aim**

The objective of these experiments was to examine the corrosion of electrodeposited technetium over an extended period.

### **2.4.2 Method**

A simulant solution was prepared that contained 3.4g of iron as ferric nitrate, 0.5g of uranium as uranyl nitrate, 2mg of strontium as strontium nitrate, 6mg of cobalt as cobalt nitrate and 20mg of ruthenium as ruthenium nitrate in 260g of sodium nitrate. The solution pH was raised to pH10.5 by addition of sodium hydroxide. A large quantity of precipitation occurred. The solution was stirred and left to stand overnight after which the supernatant liquid was filtered through a 1 $\mu$ m filter. The  $\beta/\gamma$  activity of the solution was the same as the background count for the solution without any uranyl nitrate. This solution was used as the background electrolyte for deposition/corrosion experiments.

The simulant solution was doped with pertechnetate to provide an activity of 100Bq/cm<sup>3</sup>. The solution (total volume 400cm<sup>3</sup>) was placed into a batch cell of the type illustrated in Figure 5. The working electrode was manufactured from platinised titanium and had a geometric area of 70cm<sup>2</sup>. The counter electrode was also manufactured from platinised titanium. The working electrode potential was held at -1V versus the SCE reference electrode. During this phase of the experiment, the electrodeposition process was removing the technetium from the solution. Once the electrodeposition was completed, then the electrode was removed from the container and placed into simulant that did not contain technetium. The rate of technetium deposit corrosion was measured by sampling this solution periodically and analysing the solution for technetium. The corrosion experiment was repeated with a similarly coated electrode, the voltage of which was maintained at -0.7V (versus SCE) in order to provide cathodic protection; and third experiment in which an identical electrode was placed into the technetium bearing simulant. This last experiment was performed as a blank in order to determine whether any passive adsorption was occurring.

### **2.4.3 Results**

It was possible to calculate the removal and corrosion rates and these are shown in Figure 9 and Figure 10. The adsorption results for the blank experiment are illustrated in Figure 11.

It is clear from Figure 9 that, in both experiments, the technetium was rapidly removed.

The data presented in Figure 10 indicates that over fifty per cent of the activity on the electrode had redissolved within two hours of switching off the cell current. The activity level in the solution then gradually increased to approximately 75% of the starting value after 1000 hours operation. With a cathodic protection voltage of -0.7V applied to the cell, the average amount of technetium found in the liquor was only 1% of that deposited. This indicates that the technique was extremely effective at preventing corrosion of the technetium deposit.

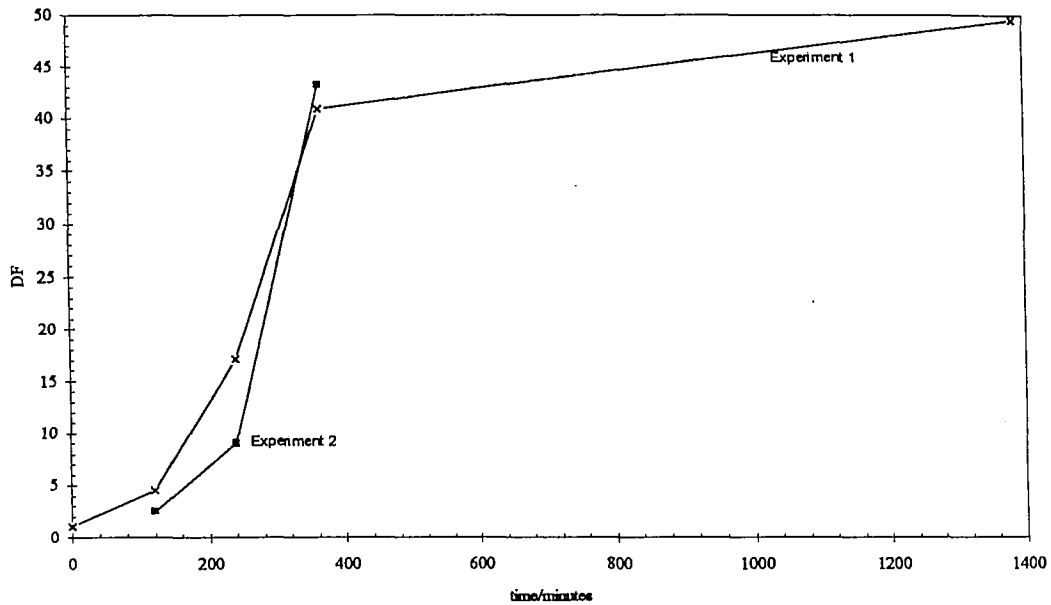


Figure 9 Variation Of Technetium DF With Time During Loading Period For Technetium Deposit Corrosion Experiments.

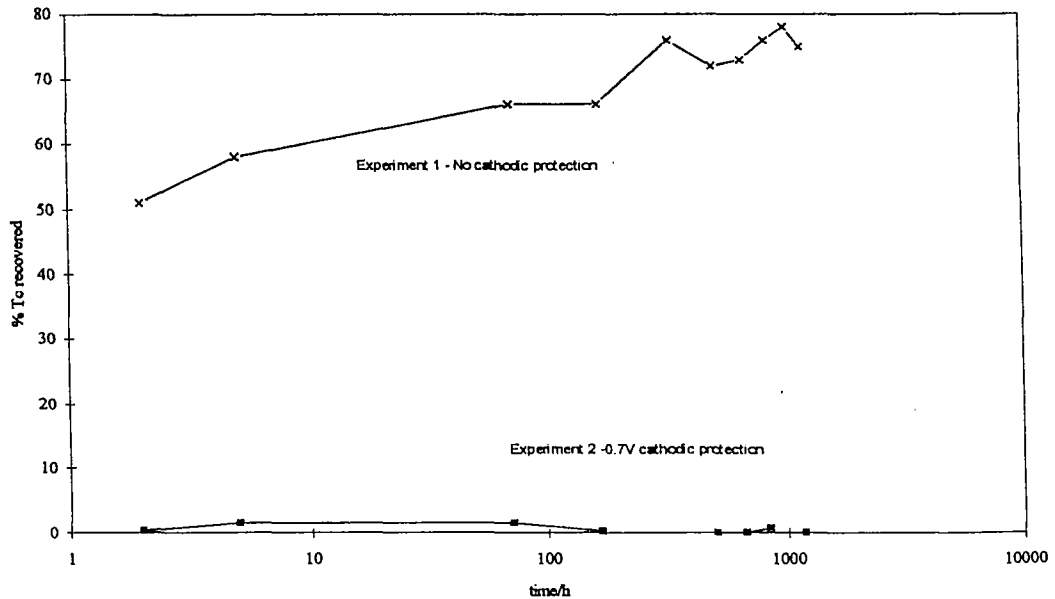


Figure 10 Variation Of Solution Technetium Content With Time During Deposit Corrosion Experiments.



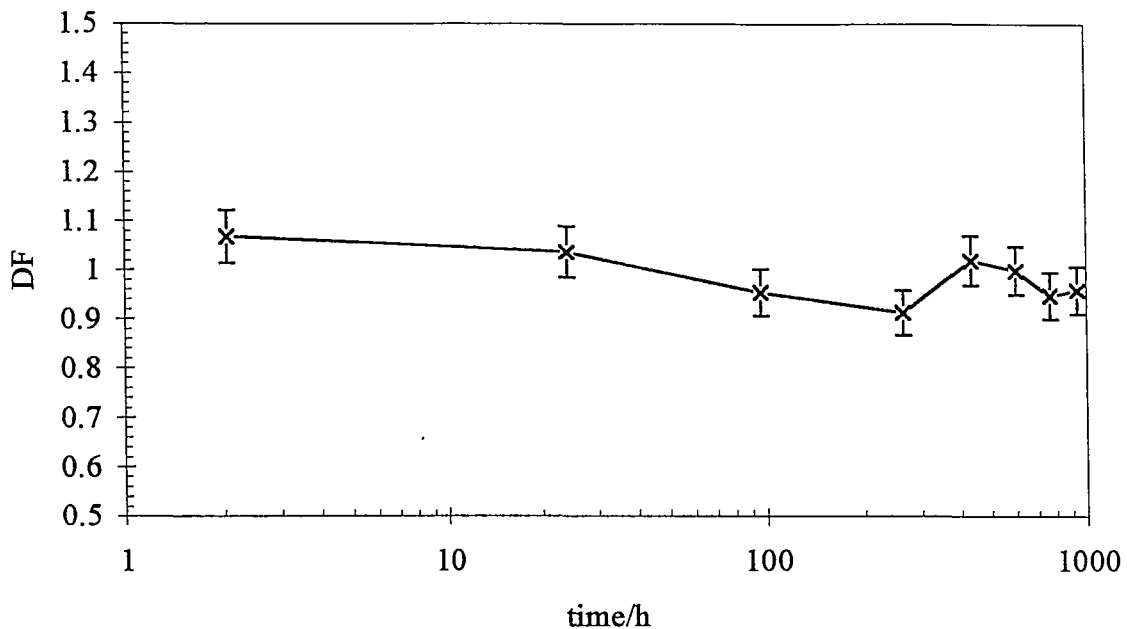


Figure 11 Determination Of Passive Adsorption Of Technetium On Electrode And Vessel.

In Figure 11, the variation of DF with time indicates that very little, if any, technetium was lost from the solution via an electrode or vessel adsorption mechanism. The average DF was 0.99 with a variation of 0.05.

#### 2.4.4 Conclusions

The results of these experiments indicate that the data obtained from the corrosion experiments can be attributed to the redissolution of the technetium deposit and that there was no competing adsorption mechanism such as onto the walls on the container. In the case where the cell was effectively switched off, nearly 80% of the technetium was found to have redissolved after 1000 hours, although nearly 50% had corroded after only 2 hours with the power disconnected. The implications of these results are that power failure to the cell should be regarded as a significant source of risk. The cathodic protection experiment indicated that a cell potential of -0.7V was sufficient to prevent the redissolution of the technetium deposit. This provides an option for a battery backup cathodic protection system in the event of external power failure, thus preventing a massive ingress of technetium into the treated stream. Such a system could also be adopted for the purposes of storage, if storage of the cells full of liquor were to be the preferred option.

## 2.5 TECHNETIUM LOADING EXPERIMENT

### 2.5.1 Aim

The objective of this experiment was to provide information on the loading of the technetium deposit onto an electrode substrate.

### 2.5.2 Method

The method adopted was to use a small batch cell containing a platinum wire electrode with a surface area of  $0.165\text{cm}^2$ . The electrode was placed into a three compartment cell with a platinised titanium counter electrode and a saturated calomel reference electrode (SCE). The small electrochemical cell was stirred using a micro-magnetic stirrer. The solution used was pH10.5  $260\text{g}/\text{dm}^3$  sodium nitrate containing approximately  $45\text{MBq}$  of  $^{99}\text{Tc}$  in  $7\text{cm}^3$  total solution volume. This activity corresponded to a concentration of  $0.135\text{M}$  technetium. The electrode potential was set to  $-1\text{V}$  versus the SCE. Samples of the electrolyte were taken for  $\beta/\gamma$  counting.

After 80 hours operation, the experiment was terminated because there was very little electrodeposition occurring. A new electrode was placed into the same solution and the experiment was repeated. Two samples of the solution were taken after 80 and 120 hours. These samples were analysed for technetium.

### 2.5.3 Results

The electrode rapidly became coated with a black deposit, indicating that electrodeposition was occurring. The variation of current density with time is illustrated in Figure 12. The current density rapidly decreased from  $3\text{mA}/\text{cm}^2$  to approximately  $0.65\text{mA}/\text{cm}^2$  after 10 hours. The current then remained constant for a period of 40 hours, after which there was a decrease to  $0.1\text{mA}/\text{cm}^2$  over a period of 10 hours.

With respect to the activity of the solution, after 50 hours the activity had decreased by 18%. After a further 20 hours there had been very little further change in the activity of the solution.

The experiment was terminated and a fresh platinum electrode was placed into the same active solution. After another 80 hours the solution activity had decreased by a further 22%. There was no change in solution activity after a further 40 hours electrolysis.

At this point, the platinum electrode was removed from the solution and a piece of carbon felt weighing  $0.033\text{g}$  was placed into the active liquor. The felt was the same type as used in the Porocell. The objective of this experiment was to determine whether passive adsorption of technetium occurred since removal of manganese under zero current conditions had been observed (see section 0). There was no change in the solution activity over a 24 hour period, indicating no passive adsorption of technetium under the conditions used.

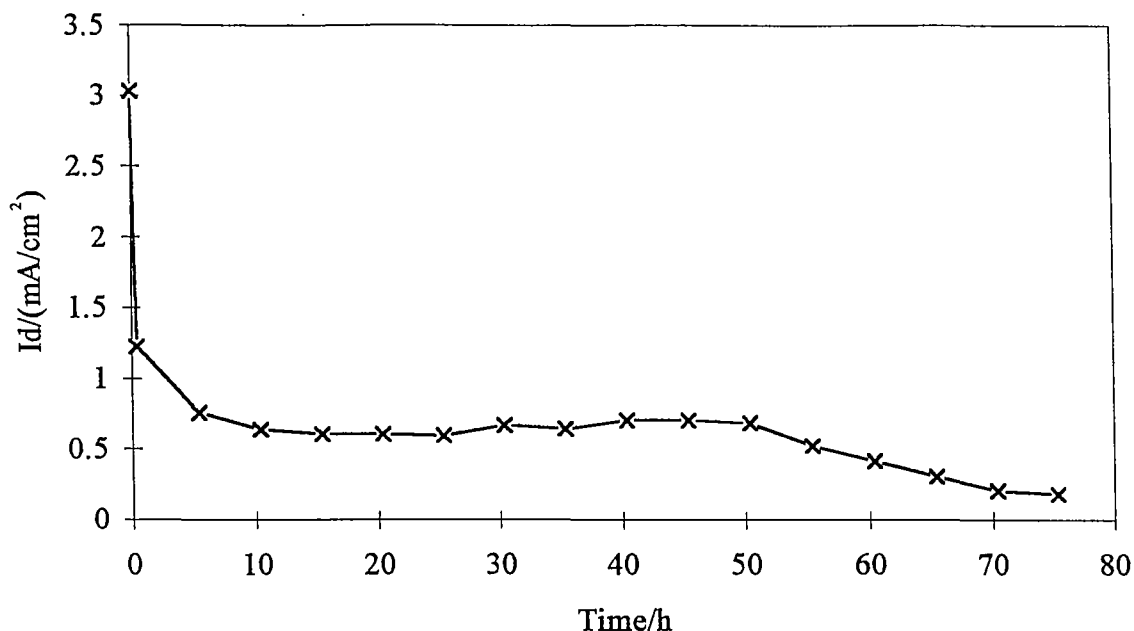


Figure 12 Variation Of Cell Current Density During Technetium Loading Experiment - Cathode 0.165cm<sup>2</sup> Platinum Wire.

#### 2.5.4 Conclusions.

The solution activity decreased by 18% during the first period of electrolysis. This corresponded to a loss of 0.17mmoles of technetium, 1.02mmoles/cm<sup>2</sup> of electrode. The weight, assuming that the deposit was technetium dioxide, was 135mg and the activity of the associated solid was 48.7MBq/cm<sup>2</sup> ( $4.87 \times 10^5$  MBq/m<sup>2</sup>). The loading for the second experiment was almost identical to that of the first.

The total charge passed during the first experiment was 52.95C. Assuming that the reduction was a three electron process, then the total amount of technetium lost from the solution should have been 0.183mmoles. The deposition was 93% current efficient under the conditions studied.

Finally, no passive adsorption of technetium occurred on a carbon felt substrate. This indicated that the pertechnetate is less oxidising than the permanganate.

## 2.6 POROCELL COMMISSIONING EXPERIMENTS

### 2.6.1 Aim

The Porocell was received from EA Technology. The aim of these experiments was to commission the cell prior to examining the performance with the proposed simulant system - permanganate reduction to manganese dioxide.

## 2.6.2 Method

A simple schematic of the Porocell is provided in Figure 13.

The cell comprised:

- (i) The electrochemical cell - an undivided cell with a dimensionally stable anode (DSA) and a carbon felt cathode (18cm x15cm x1cm) in the form of a cylinder. A helical copper electrode was used as a contact to the cathode. The form of the cathode was similar in concept to a cartridge filter, inasmuch as the solution was forced through the side walls of the electrode cylinder.
- (ii) A reservoir that enabled a range (1-4dm<sup>3</sup>) of solution volumes to be treated in recirculation mode.
- (iii) A pump that was capable of pumping at over 300dm<sup>3</sup>/h.
- (iv) Various taps and valves for solution flow control.
- (v) A flow meter (nominally rated 0-320dm<sup>3</sup>/h).

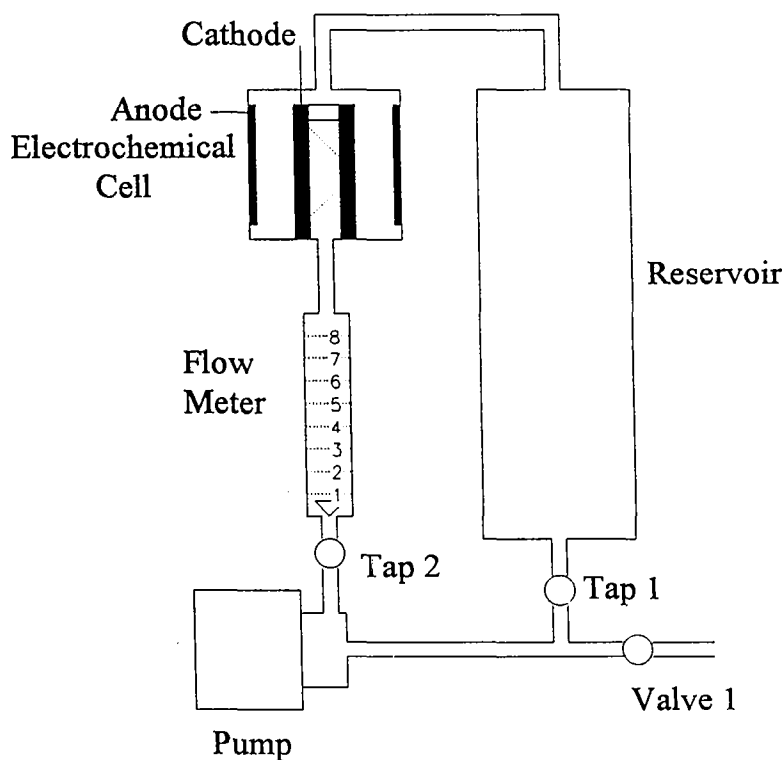


Figure 13 Schematic Of Porocell.

Solution flow was from the pump through the flow meter to the electrochemical cell. The solution entered through the base of the carbon fibre cylinder and was then forced to exit this

cylinder via the side walls since the other end of the cartridge was blocked by a plastic stopper. The liquid then exited the electrochemical via the top and passed into the reservoir and from there back to the pump.

The solutions used in the commissioning experiments were 0.1M sodium sulphate with 10mM sulphuric acid. These solution were doped with copper sulphate to provide an electroactive species. The solution flowed through the electrochemical cell at a rate of 60dm<sup>3</sup>/h. The cell was connected to a potentiostat with the carbon fibre electrode acting as the working electrode, the DSA as the counter electrode and a saturated calomel electrode was inserted into the flow loop to act as the reference electrode. Linear sweep voltammograms were taken by slowly increasing the cathodic potential applied to the working electrode. The potential sweep rate was 10mV/minute.

### 2.6.3 Results

The linear sweep voltammograms were recorded with three different solutions being recirculated through the cell, the background electrolyte, the background electrolyte containing 100ppm copper (as sulphate) and the same electrolyte containing 500ppm copper (as sulphate). The variation of current with potential is illustrated in Figure 14 - the current associated with the background electrolyte has been subtracted to provide only the currents associated with copper reduction.

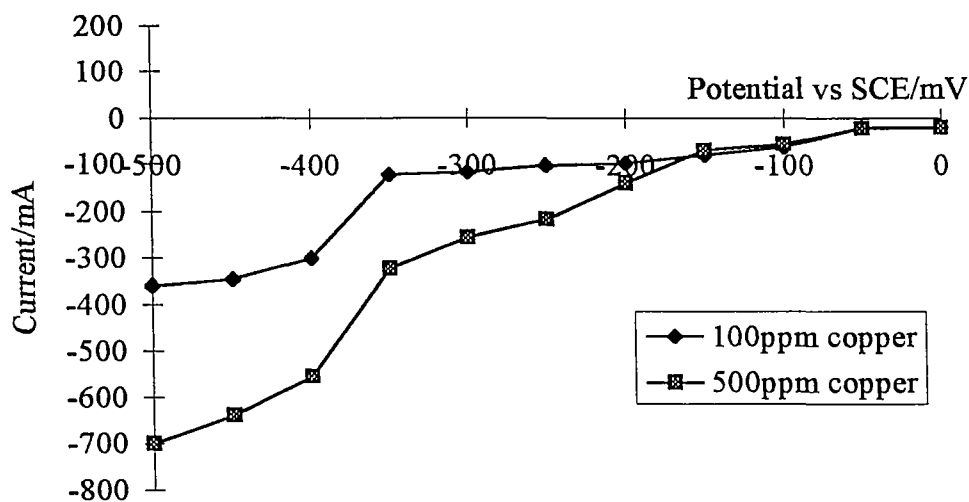


Figure 14 Linear Sweep Voltammogram For Copper Removal Using The Porocell.

### 2.6.4 Conclusions

The results indicate that the reduction process occurs in two stages. The currents associated with each stage are similar. This would indicate two single electron reduction processes

(Equation 2). For copper reduction, this reaction is well known in chloride media - but is somewhat surprising in sulphate.



An alternative explanation would involve two different electroactive sites on the carbon.

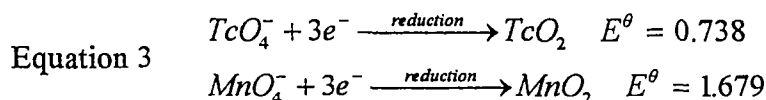
With respect to the rate of copper recovery, the reduction current of 700mA represents a removal rate 0.84g of copper per hour. This is for an electrode with a nominal surface of 270cm<sup>2</sup>.

No physical problems occurred during the commissioning of the cell.

## 2.7 POROCELL PERFORMANCE EXPERIMENTS

### 2.7.1 Aim

The objectives of these experiments was to provide an indication of the performance of the cell with an inactive “pertechnetate simulant” solution. The simulant used contained permanganate as the target species (Equation 3).



The E<sup>θ</sup> values are potentials in volts with respect to the normal hydrogen reference electrode. Thus, permanganate is more oxidising than pertechnetate, but both can form an insoluble metal dioxide on reduction from oxidation state 7 to oxidation state 4.

### 2.7.2 Method

A simulant solution containing 260g/dm<sup>3</sup> of sodium nitrate, adjusted to pH10.5 with sodium hydroxide was used for these experiments. Potassium permanganate was added to provide the appropriate manganese concentration. The solution was placed into the reservoir and recirculated through the electrochemical cell at a rate of 30dm<sup>3</sup>/h. Samples were collected after the electrochemical cell for analysis using atomic absorption spectroscopy. The carbon felt electrode was removed from the cell at the end of each experiment and soaked in 1M hydrochloric acid to dissolve the manganese dioxide.

The experiments were performed in the order described below, that is 0.5A-2A (manganese concentration of 300ppm), 0.05A to 0.2A (manganese concentration 10ppm), passive adsorption (manganese concentrations ranging from ~10ppm to 100ppm). The passive adsorption experiments were performed in order to provide an explanation of the results obtained during the reduction experiments at cell currents ranging from 50mA to 2A.

### 2.7.2.1 Cell currents 0.5-2A

The current required to reduce 300ppm Mn(VII) to Mn(II) in a solution volume of 3dm<sup>3</sup> within 1 hour is 1.3A at one hundred per cent current efficiency. Thus, these experiments were performed with a total liquor volume of 3dm<sup>3</sup>, the stream contained approximately 300ppm manganese with sampling every sixty minutes.

### 2.7.2.2 Cell currents 0.05-0.2A

The current required to reduce 10ppm Mn(VII) to Mn(II) in a solution volume of 4dm<sup>3</sup> within 1 hour is 58mA at one hundred per cent current efficiency. These experiments were performed with a total liquor volume of 4dm<sup>3</sup>, the stream contained approximately 10ppm manganese with sampling every fifteen minutes.

### 2.7.2.3 Cell current 0 Passive Adsorption.

These experiments were performed with a total liquor volume of 4dm<sup>3</sup>, the stream contained 20-100ppm manganese.

### 2.7.3 Results

The results of these experiments are illustrated in Figure 15 to Figure 17.

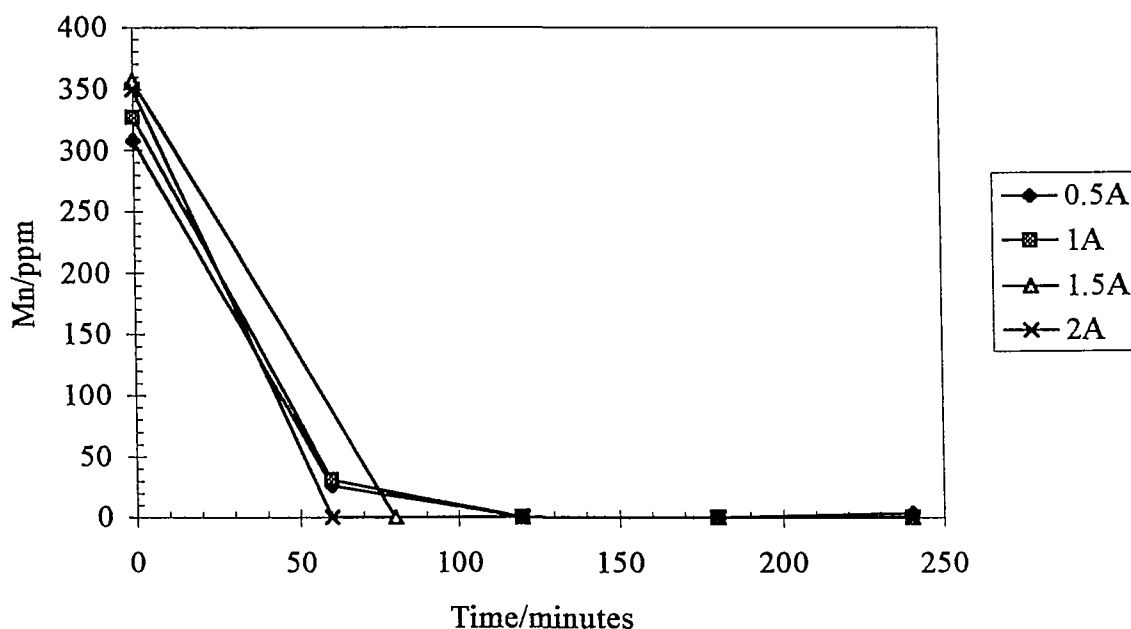


Figure 15 Manganese Removal Using The Porocell (details in text).

From the figure above, it can be seen that the concentration of manganese in the simulated waste was rapidly reduced from approximately 300ppm to less than 50ppm within sixty

minutes for all the cell currents tested. This represents greater than 100% current efficiency for the tests performed at both 0.5A and 1A. Within 120 minutes the concentration of manganese in the treated liquor was less than 1ppm - a decontamination factor of >300.

The amount of manganese dioxide on the felt at the end of the experiments represented 55% (@0.5A), 57% (@1A), 59% (@1.5A) and 58% (@2A) of the total manganese in the system. The remaining manganese was in the form of manganese dioxide that was being recirculated via the reservoir.

From the figure below, it can be seen that the concentration of manganese in the simulated waste was rapidly reduced from approximately 10ppm to less than 2ppm within twenty minutes for all the cell currents tested. This represents greater than 100% current efficiency for the tests performed at both 50mA and 100mA. Within 40 minutes, the concentration of manganese in the treated liquor was less than 1ppm - a decontamination factor of >10. The rate of removal decreased with increasing current.

The amount of manganese dioxide on the felt at the end of the experiments represented 53% (@50mA), 93% (@100mA), 73% (@200mA) of the total manganese in the system. The remaining manganese was in the form of manganese dioxide that was being recirculated via the reservoir.

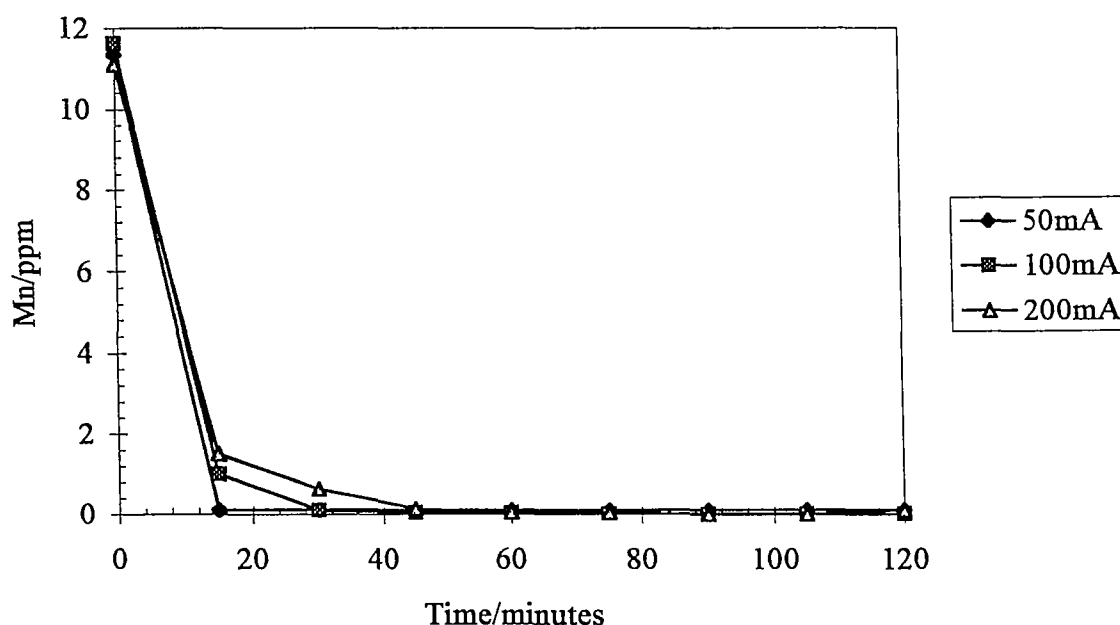


Figure 16 Manganese Removal Using The Porocell (details in text).



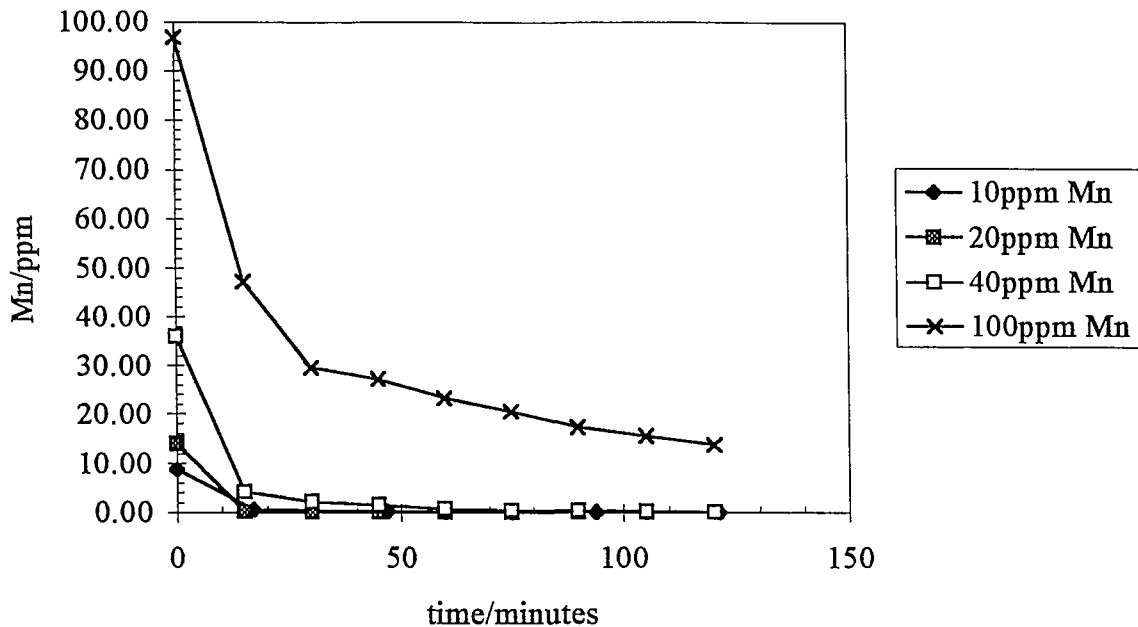


Figure 17 Passive Adsorption Of Manganese With Porocell.

From Figure 17, it can be seen that manganese was rapidly adsorbed from the solution. For a starting concentration of <20ppm manganese, the manganese concentration in the solution was found to be <1ppm after 15 minutes. At the highest concentration studied (100ppm manganese), the adsorption process became very slow when the amount remaining in solution was 20ppm, thus 80% of the manganese had been adsorbed.

Acid treatment of the treated solution and the felt provided evidence for an acid soluble manganese compound in the treated stream. At 100ppm Mn, this represented 17% of the manganese removed from the system.

#### 2.7.4 Conclusions

The results from these experiments indicate that the removal process involves a combination of adsorption and reduction. It is also clear that the adsorption route involves some form of chemical reaction, since an insoluble manganese compound (presumably dioxide) was formed during the passive experiments.

It is not possible to distinguish between the adsorption route and the electrochemical reduction mechanism for the low manganese concentrations (<40ppm).

## 2.8 POROCELL LOADING EXPERIMENT

### 2.8.1 Aim

The objective of this experiment was to determine the maximum loading of manganese dioxide that the Porocell could support whilst maintaining the processing performance.

### 2.8.2 Method

A schematic of the Porocell set up is shown in Figure 18. A concentrate solution of potassium permanganate (2000ppm Mn) was fed into the main reservoir at a rate of 100cm<sup>3</sup> per hour. The solution in the main cell was 4 dm<sup>3</sup> of pH10.5 260g/dm<sup>3</sup> sodium nitrate. The main solution was recirculated through the cell at a rate of 100dm<sup>3</sup>/h. The weir was placed in the system in order to provide a bleed point, such that the solution volume was maintained during the course of the experiment. The cell current was set at 1A. The rate of addition of manganese was 0.2g/h, that is 3.63mM/h. At this rate of addition, the current required for the reduction from permanganate to manganese dioxide would have been 292mA. The cell current assumed that the current efficiency for the electrochemical reaction would be approximately 30%.

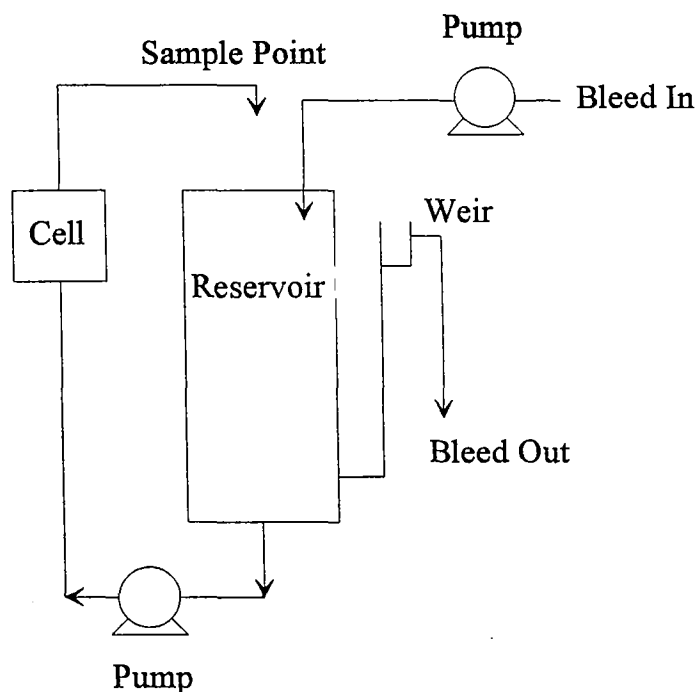


Figure 18 Porocell Set Up For Loading Experiment.

The cell was operated, and samples were taken, over a period of 115 hours. After 155 hours it was noted that a large amount of manganese dioxide was being pumped around the system. It was assumed that the self filtering nature of the Porocell had failed and the experiment was stopped.

The cell was dismantled and the manganese content of the various components was determined by dissolving the oxide in hydrochloric acid.

### 2.8.3 Results.

The cell voltage remained fairly constant throughout the experiment at 2V ( $\pm 0.1V$ ). Several samples of the recirculating solution were taken from the sampling point (after the

electrochemical cell and before the reservoir) for manganese analysis. The variation of soluble manganese content in the samples with time is illustrated in Figure 19.

The distribution of manganese throughout the system is provided in Table 1. We can see from the table that approximately three quarters of the manganese was found on the electrode. The electrode geometric area was  $226\text{cm}^2$  and thus the loading was  $84\text{mg}/\text{cm}^2$ .

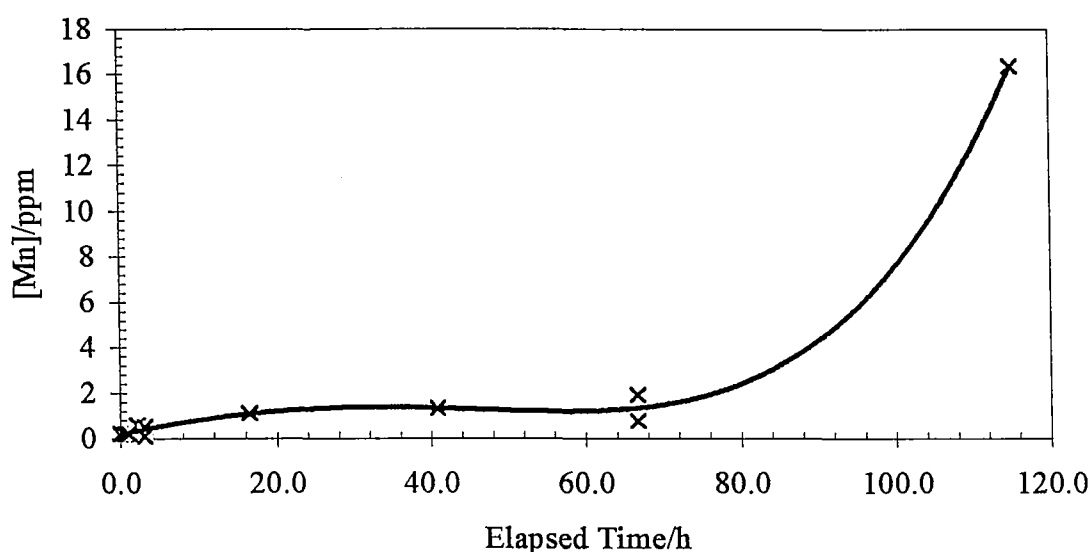


Figure 19 Variation Of Manganese Concentration With Time During Loading Experiment.

#### 2.8.4 Conclusion.

The manganese content in the recirculating waste remained fairly constant at approximately 1ppm for at least the first 70 hours of this experiment. The rate of rate of addition of manganese into the solution would represent the treatment of  $4\text{dm}^3$  of 50ppm manganese every hour, with a decontamination factor of fifty being maintained.

There are several risks associated with the translation of these results into technetium equivalents.

- (i) The electrochemical properties of the pertechnetate and the permanganate, although similar, are not identical.
- (ii) There may be different performances in terms of loading.
- (iii) Is the comparison to be made on the basis of weight, number of moles deposited or layer thickness?

- (iv) What is the nature of the deposited species  $MnO_2$ , Mn,  $TcO_2$ , Tc, mixtures of oxides and metals or other oxy-metal species?

Having indicated that there are risks associated with the calculation, we shall assume that the permanganate and pertechnetate behaviours are identical, and that the loading capacity is based upon weight, and that the species deposited is the metal dioxide. Thus the electrode loading is  $84mg/cm^3$  since the felt has a thickness of 1cm. This loading represents  $0.64 \times 10^{-3}$  moles of technetium per cubic centimetre of felt. From a radiological viewpoint, this loading corresponds to  $3.05 \times 10^7$  Bq per cubic centimetre of felt.

Table 1 Mass Balance For Manganese During Deposition.

Sample	Mn/mg	Per Cent
Solution fed into experiment	22401	-
Manganese recovered from electrode	17073	76.2
Manganese recovered as solid from main stream	2290	10.2
Soluble manganese in main stream	114	0.5
Soluble manganese in bleed	1.62	0.007
Manganese recovered as solid from bleed waste	1200	5
Total	20565	92

# 3. Conclusions

## 3.1 SUMMARY

### 3.1.1 Cathode Corrosion

The cathodes were tested in pH10.5 260g sodium nitrate. The electrochemical potential of the cathode was set at -1V versus SCE. There was visible evidence of significant corrosion of the mild steel electrode, with some corrosion of the stainless steel electrodes (type 304 and 316) also being noted. There was no discernible evidence of corrosion of the platinised titanium cathode. From the magnitude of the cell currents it was concluded that there was significant electrocatalytic activity on the mild steel and platinised titanium electrodes although no attempt was made to identify the electrochemical reactions occurring on these electrodes.

### 3.1.2 Technetium Removal Kinetics

The five selected electrode materials were used as cathodes in a three electrode cell. The electrode potential of all the electrodes was set at -1V versus SCE. The steels (mild, and both stainless steels) exhibited very similar technetium removal properties - a decontamination factor of approximately 10 after 6 hours. Electrodes constructed from platinised titanium and carbon were more effective than the steels for the decontamination reaction, with DFs of approximately 35 being observed for both materials after six hours treatment.

### 3.1.3 Technetium Coating Corrosion.

A more complex simulant was used in these experiments. An electrode was coated with a technetium deposit and then the power supply was disconnected. Within 2 hours nearly fifty percent of the activity associated with the technetium deposit had redissolved. In the next 1000 hours the amount of activity in the solution increased to eighty per cent of that originally deposited. The application of a cathodic protection potential of -0.7V almost completely inhibited the corrosion of the technetium deposit. Blank experiments indicated that no technetium was lost from the system by routes associated with adsorption.

### 3.1.4 Technetium Loading.

Using a small piece of platinum wire as the cathode we found that the maximum amount of technetium that could be deposited onto the electrode was approximately  $4.87 \times 10^5$  MBq per square metre of electrode.

### 3.1.5 Porocell Experiments.

The Porocell was commissioned and operated with manganese in the form of permanganate as an inactive simulant for technetium. We found that the accuracy of the simulation (Mn for Tc) was limited by a degree of catalytic permanganate reduction, whereas the analogous reaction

of pertechnetate did not occur. However, the cell was extremely effective at removing manganese from the solution, 300ppm to less than 1ppm. Nearly sixty per cent of the manganese was found on the electrode, the remainder was being recirculated around the cell. A batch cell loading experiment was performed in which the manganese removal rate was maintained at 50ppm Mn in four litres per hour (0.2g manganese per hour). The concentration of manganese remained below 1ppm (DF 50) for over 60 hours. The final loading of manganese 84mg/cm<sup>2</sup> of geometric electrode area.

## 3.2 CONCLUSIONS

This phase of the programme was set several objectives:

- To take delivery of a "Porocell" type electrochemical unit from EA Technology, to commission and to test this cell that is compatible with disposal drum geometry.

The Porocell has performed well in the task of removing manganese (in the form of permanganate) from an EARP simulant stream to generate a secondary waste of solid manganese dioxide. The cell was operated in a batch mode, that is in the same way as would need to be operated on genuine waste which is generated in batches. Assuming a starting concentration of 50ppm, DFs in excess of fifty were continuously achieved at an effective waste throughput of four litres per hour. Most of the manganese dioxide was found to be located on/in the electrode, although a significant quantity (depending upon conditions) was found to be recirculating around the batch system. The maximum loading (84mg/cm<sup>2</sup> geometric electrode area) was determined by the apparent failure of the cylindrical electrode to act as a filter. Thus, post cell filtration will be required and may well have increased the operational lifetime of the electrodes.

The cell geometry is cylindrical and thus compatible with drum disposal. The cell dimensions were fixed at 19cm high and a diameter of approximately 15cm. A comparative schematic with a 560 litre waste drum is shown in Figure 20. Based upon external dimensions, the cell is approximately 1/5 the diameter and 1/7 the height of the drum - almost 1/186 of the total volume. These experiments did not address the aspect of the variation of loading performance with cell volume. It would not be unreasonable to conclude that the loading would increase in proportion to the electrode height, given a fixed diameter. It is not possible to draw any conclusions about the variation of loading with electrode cylinder diameter.

- To confirm the validity of the redissolution measures tested in the previous phase and to test several cathode materials.

The corrosion protection methodology was tested over a period in excess of 1000 hours. An electrode potential of -0.7V (vs SCE) was sufficient to prevent redissolution of the technetium coating. The biphasic release of technetium corrosion process in the absence of cathodic protection may indicate the presence of two forms of technetium. The least stable of which corroded quite rapidly, thus necessitating the use of the cathodic protection method for any operational plant. It was also evident that adsorption played no role in these results.

The experiments also investigated the variation of rate of technetium removal with cathode material. We found that platinised titanium and carbon provided the best performance. These results are fortuitous given that the Porocell routinely operates with a relatively inexpensive carbon felt cathode.

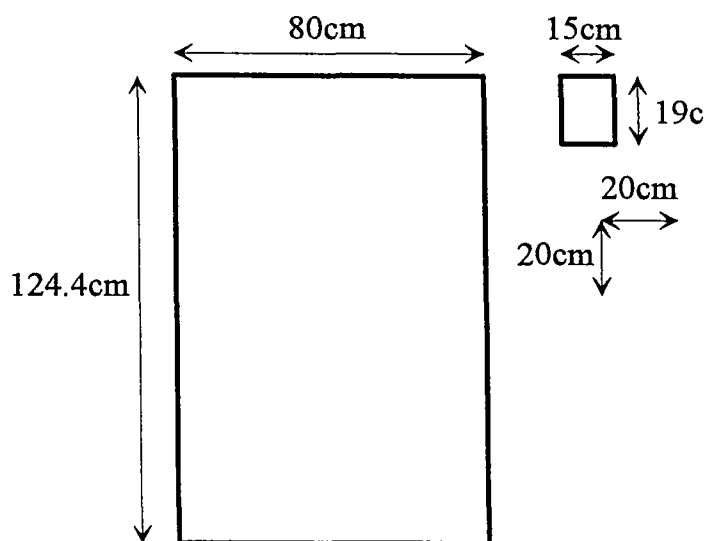


Figure 20 Relative Scale Of Disposal Drum and Experimental Porocell.

- To establish the maximum loading capacity of the electrochemical system, given certain performance criteria.

The active loading capacity experiment was performed using a very small platinum electrode - area  $0.165\text{cm}^2$ . It was necessary to operate at this scale to minimise operator dose. After 50 hours operation the technetium content of the liquor had been reduced by 18% and little further electrodeposition was observed during subsequent electrolysis. Replacement of the electrode with a fresh electrode resulted in further electrodeposition. The maximum loading on the platinum electrode was 135mg of technetium dioxide per square centimetre of electrode. This corresponded to  $4.86 \times 10^{11}\text{Bq}$  per square metre. It was not possible to determine the surface area of the carbon felt used in the Porocell, although we did confirm that the technetium did not adsorb on the felt cathode under zero current conditions.

### 3.3 IMPLICATIONS

This phase of the programme has confirmed that the Porocell type system can be used to remove a species from solution that is electrodeposited in the form of an oxide on a cathode. We have demonstrated that decontamination factors for such reactions can be very high - in excess of 300 and easily in excess of fifty. By assuming that the technetium performance is similar to that of the manganese, we can estimate that 125 1.5m Porocell cells would be required to provide a decontamination factor of fifty on a batch of feed flowing at  $4\text{m}^3/\text{h}$ . As indicated above, we have no information on the variation of performance (rate of decontamination or loading) with electrode diameter. It will be necessary to either obtain this information from EA Technology, or to confirm this characteristic by experiment.

The cell acts, to an extent, as a filter; but the filtration process is not completely effective and an insoluble oxide was recirculated through the system. In an active situation this spalling would need to be prevented since the loose dioxide may redissolve, thus reintroducing activity to the stream.

We have identified that, under the conditions studied, there is a limit to the deposition process, with the maximum loading corresponding to  $4.87 \times 10^5$  MBq per square metre of electrode. From Figure 1, the technetium content of the stream is 200000Bq/ml. Thus, 1 square metre of electrode would process  $2.4\text{m}^3$  of waste. Inactive studies with permanganate also identified a loading limit - although this may have been caused by a physical failure of the electrode as opposed to a limitation imposed by the electrochemical properties of the deposit. It was not possible to determine the available electrode area of the felt used in the Porocell. At some stage it will be necessary to repeat this experiment with a piece of the felt in order to provide loading information on the high surface area material.

With regards to electrode materials, carbon performed as well as any of the materials tested. The disposal of such an electrode would need to be investigated since there is a limit on the level of organic species that can be present in disposal drums.

### **3.4 FUTURE WORK**

A proposal relating to active operation of the Porocell has already been submitted. It is not possible to perform active loading experiments on the Porocell in the Supervised Area proposed for this work. It would be possible to perform such experiments in hot cells available elsewhere on the Harwell site, but this would represent a significant added expense.

In the proposal, we have suggested that cell should be operated with different cathode types, depending upon disposal considerations. These tests could be performed with different felt thicknesses in order to provide information on performance with change in geometry. Once again, however, active loading experiments would require specialist laboratory facilities.

The final area that needs to be addressed is the prevention of material spalling from the electrode. It may be possible to use a Porocell downstream of the main unit that contains a more effective carbon filter, or to use conducting filter material, a Carbosep type filter for example, that can be biased to provide a cathodic filtration zone.