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The Removal of Technetium from EARP Waste Streams, Phase II

AEA Technology

R&D Technical Report P50

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The Removal of Technetium from EARP Waste Streams, Phase II

P.A. Fletcher, C.P. Jones, A.D. Turner and P.F. Rayment

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Statement of use
This report contains information which will assist in the assessment of options open to BNFL for treating EARP waste in the medium and long term, and point the direction for further research and development effort. A third phase programme, again involving both AEA Technology and BNFL Sellafield, is already in progress.

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R&D Technical Report P50

Executive Summary

During the first phase of the experimental programme a number of techniques were compared for the removal of the soft β emitter ^{99}Tc from a simulant stream ($\approx$ 50Bq/cm^3 ^{99}Tc as pertechnetate in 27g/dm^3 sodium nitrate pH10). Of the methods examined (electrochemical ion exchange (EIX), seeded ultrafiltration (UF), homogeneous reduction and electrochemical reduction) the best results were obtained by direct electrochemical reduction of the pertechnetate anion to insoluble technetium dioxide. The objective of this first phase was to obtain a decontamination factor (DF) in the range of 5 - 10.

The simple simulant waste used during these trials contained only pertechnetate and sodium nitrate (at pH10). Another significant species present in the simulant waste - ^{106}Ru - may also be removed from the stream as an insoluble oxide during electrochemical processing or may even interfere with the technetium reduction process. This second phase of the programme was designed to investigate the electrochemical removal of this species in tandem with the electrochemical reduction of the pertechnetate. During this part of the programme it was also necessary to establish whether corrosion of the technetium deposit occurred and if so how to minimise the effect by the application of suitable simple "down-time" storage techniques. Upon successful completion of the simulant work, the aim was to perform simple benchtop scale experiments on a genuine stream at BNFL Sellafield.

The following represents a summary of the results obtained during the programme.

Interference experiments:

Sr	There was no noticeable effect on Tc removal and no change in Sr concentration.
Sb	There was no noticeable effect on Tc removal and no systematic change in Sb concentration.
Ru	For high levels of Ru, the Ru removal preceded Tc removal (Ru DF >23). At realistic levels of Ru, the induction period was so short as to be difficult to measure.
Mixture	Short induction period, however Tc removal to DFs >30 still obtained.

It should be noted that as with Phase I, the target DF for the process was between 5 and 10.

Redissolution experiments:

Power off	Tc coating redissolves slowly in feed.
Cathodic protection -0.4V	Tc coating redissolves slowly in feed.
Ar saturation (deO$_2$)	Tc coating redissolves slowly in feed.
Cathodic protection -0.6V	Tc coating redissolves slowly (<-0.4V).
Cathodic protection -0.675V	Very slow, almost inhibited redissolution.

An alternative option is to empty the cells when not in use or under "power down" conditions.

Genuine Waste:

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). The ruthenium DFs were more disappointing - although this may have been as a result of not filtering the waste after electrolytic treatment.

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THE REMOVAL OF TECHNETIUM, RUTHENIUM STRONTIUM AND ANTIMONY FROM THE E.A.R.P. EFFLUENT STREAM.

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. A typical proportionation of the activity in MAC is given in figure 2.
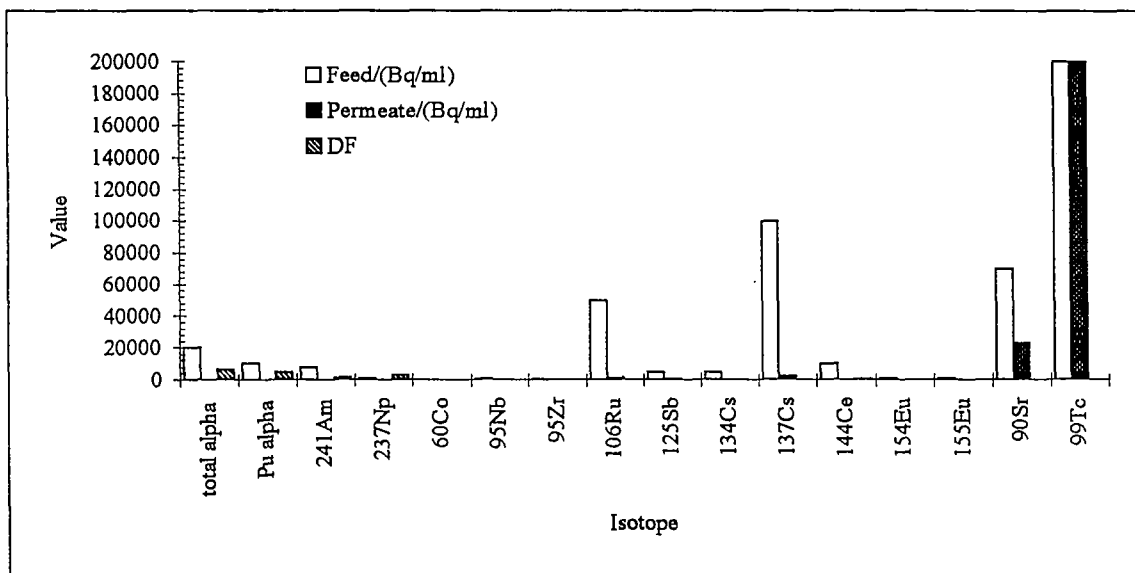
Figure 1. Variation in Feed activity, permeate activity and decontamination factor during EARP treatment of MA type stream.

EARP was conceived to primarily remove α activity from Sellafield discharges and is now performing this task well. The opportunity was also taken to significantly reduce β/γ discharges where this can be reasonably achieved. Figure 1 illustrates typical results achieved. The question now arises as to whether further reductions can be achieved on a cost effective basis. The major species remaining can be seen in figure 2 and their typical current decontamination factors (DFs) are ^{99}Tc(1), ^{90}Sr(3), ^{106}Ru(40) and ^{137}Cs(40).

Legend:
- Remainder (0.24%)
- 106Ru (0.55%)
- 137Cs (1.1%)
- 90Sr (10.25%)
- 99Tc (87.8%)
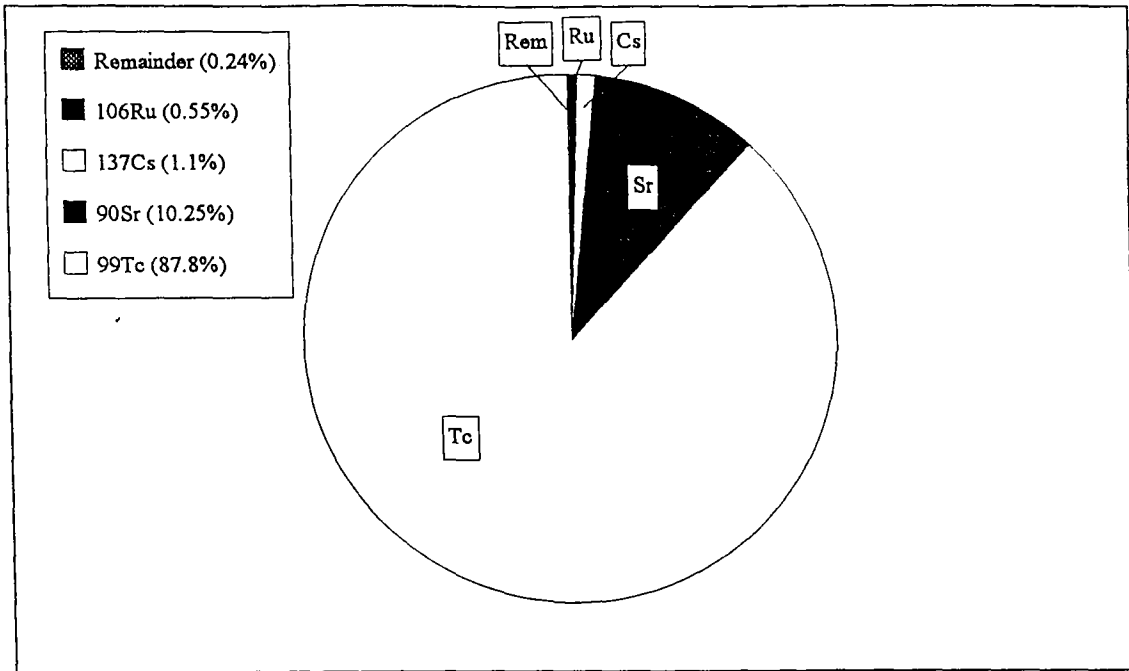
Figure 2. Activity content of liquor after EARP treatment of MA type stream.

The figures above give details of the active components only. In table 1, the inactive components present in such a feed are presented. The solution would then be treated by neutralisation to pH10.5 - followed by the addition of nickel ferricyanide - and stirred for one hour before filtration.

During the first phase of the experimental programme a number of techniques were compared for the removal of the soft β emitter ^{99}Tc from a simulant stream ($\approx$ 50Bq/cm^3 ^{99}Tc as pertechnetate in 27g/dm^3 sodium nitrate pH10). Of the methods examined (EIX, seeded ultrafiltration, homogeneous reduction and electrochemical reduction) the best results were obtained by direct electrochemical reduction of the pertechnetate anion to insoluble technetium dioxide.

The simple simulant waste used during these trials contained only pertechnetate and sodium nitrate (at pH10). Another significant species present in the simulant waste - ^{106}Ru - may also be removed from the stream as an insoluble oxide during electrochemical processing or may even interfere with the technetium reduction process. This phase of the programme was designed to investigate the electrochemical removal of this species in tandem with the electrochemical reduction of the pertechnetate. Upon successful completion of the simulant work, benchtop scale experiments were then performed on a genuine stream at BNFL Sellafield.

Table 1. Summary of EARP MAC Inactive Composition.

Species	Concentration Range	Recommended Simulant	Source Material
HNO_3 (M)	7.5 - 8.3	7.5	HNO_3
Na (g/dm³)	3 - 7	3.1	$NaNO_3$
Fe (g/dm³)	1.6 - 4.6	1.7	$Fe(NO_3)_3$
U	470 - 1000	550	$UO_2(NO_3)_2$
Cr(III)	260 - 640	260	$Cr(NO_3)_3.9H_2O$
Cr(VI)	0 - 380	20	CrO_3
Ni	160 - 530	160	$Ni(NO_3)_2.6H_2O$
K	22 - 100	26	KNO_3
Ca	100 - 380	145	$Ca(NO_3)_2.4H_2O$
Mg	30 - 40	30	$Mg(NO_3)_2.6H_2O$
Al	15 - 40	15	$Al(NO_3)_3.9H_2O$
Pb	180 - 340	320	$Pb(NO_3)_2$
Zn	10 - 50	10	$Zn(NO_3)_2.6H_2O$
Mn	20 - 80	25	$Mn(NO_3)_2.4H_2O$
Mo	5 - 30	30	$Na_2MoO_4.2H_2O$
Sr	1	1	$Sr(NO_3)_2$
Co	2 - 10	3	$Co(NO_3)_2.6H_2O$
Sn	0 - 1	0.0	----
Cu	10	10	$Cu(NO_3)_2.3H_2O$
SO_4^{2-} (g/dm³)	2 - 3	2	Na_2SO_4
PO_4^{3-}	300 - 400	330	H_3PO_4
TBP	5 - 60	15	TBP (l)
DBP	20 - 60	30	DBP (l)
OK	0 - 50	5	OK(l)
All figures in ppm unless specified			
Volume 1800m³/y (2 - 4m³/h batch), Permeate pH 10.5			

It is anticipated that the electrochemical system should function in a batch mode. In periods where the unit is not operational, corrosion of the plated active oxide could cause a very serious contamination of subsequent streams. During this phase of the programme it was necessary to establish whether corrosion does occur and if so can it be minimised by the application of suitable simple "down-time" storage techniques.

1.2. Outline Development Programme.

An organisation chart is provided below (figure 3) to illustrate the experimental sub-programmes. Once the electrochemical cell had been designed and constructed it was then tested for the removal of technetium from a stream in the presence and absence of ruthenium, strontium and antimony. These components were added as inactive species and analysed by ICP MS (inductively coupled plasma mass spectroscopy). Upon successful completion, these experiments were then extended to a simulant containing other inactive components (and uranium) after a flocculation and filtration had been

performed. These experiments were followed by an electrode loading test in which the rate of redissolution was studied by monitoring the rate of increase in solution activity after loading and switching off the power to the cell. In the absence of serious problems during these runs, the experiments were then repeated at Sellafield using genuine treated MA type waste.

2. HARWELL EXPERIMENTAL PROGRAMME.

2.1. Introduction

The results discussed in this section relate to experiments performed at Harwell. The trials on genuine MAC permeate are described in section 3. In phase I of the programme, it was shown that it was possible to remove technetium from an aqueous stream by reduction of pertechnetate to insoluble technetium dioxide. The simulant stream was very simple - containing only ammonium pertechnetate and $27g/dm^3$ sodium nitrate (pH10). In this second phase of the programme, several benchtop studies have examined the removal of technetium in more realistic simulants ($\approx$ $260g/dm^3$ sodium nitrate, pH10.5 and selected species from table 1). The interference of active species of special interest (ruthenium, strontium and antimony) and major inactive species (iron, uranium, phosphate and tri-butyl phosphate) on the technetium decontamination process have been studied. Simple loading experiments and "power off" experiments have been performed to examine the behaviour of the process over longer periods and any corrosion of the plated active dioxide that might result in a redissolution of the activity and major recontamination of the system.
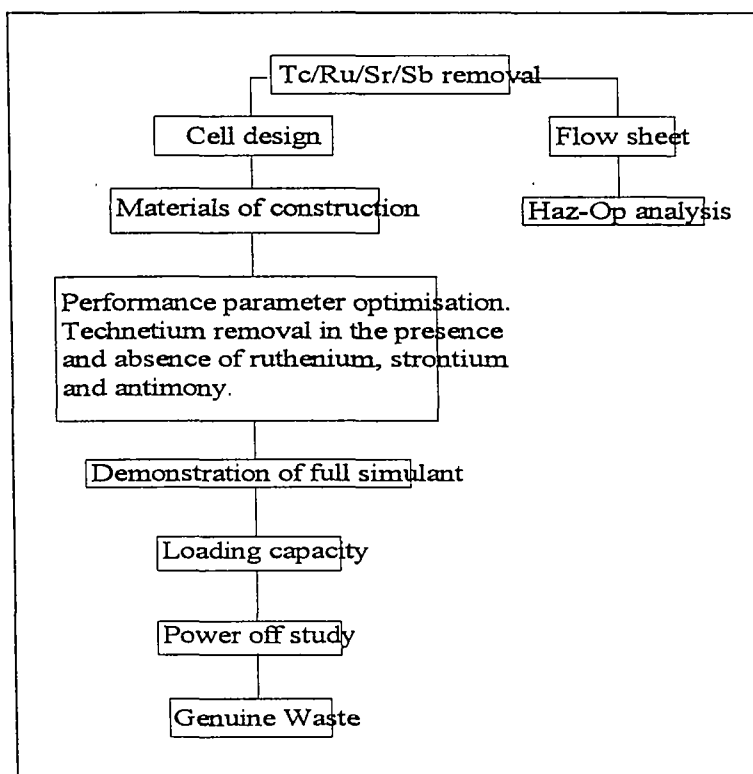
Figure 3 Programme Diagram.

2.2. Experimental and Results

2.2.1. Equipment Requirements

After careful consideration and consultation with BNFL and HMIP an electrochemical cell was selected - this cell is illustrated in figure 4.

In this cell a stainless steel cathode is used as the working electrode (total surface area $157cm^2$) and platinised titanium as the anode. The reference electrode (saturated calomel electrode SCE) is contact to the bulk liquor by means of a Luggin capillary that prevents contamination of the cell by chloride.

The value of the electrode surface area was calculated by considering the geometry of the stainless steel mesh. For the type 304, 100 mesh type electrode used in these experiments, the "real" surface area is approximately 26% greater than the geometric area as calculated from the projected surface area of a two sided planar solid of the same dimensions. A finer mesh size would result in an increase in available surface area, whereas a coarse mesh has a smaller surface area.

Testing of the cathode material was conducted in 250 cm^3 of 50 Bq cm^{-3} (8.375×10^{-7} M ^{99}Tc) simulant in the cell shown in Figure 4. A magnetic stirrer and bead were used to induce forced convection within the cell. The potential of the working electrode was then held constant (-1.00V) with respect to the SCE and samples taken at regular intervals over a period of 300 min. The residual activity for each sample was then determined by a β counting system on 0.5 cm^3 of solution evaporated to dryness on an aluminium planchette (B.S. 3775 Type 25 RA). The decontamination factor (DF) was calculated according to:

$$DF = \left(\frac{c_{st} - c_{bk}}{c_s - c_{bk}} \right)$$

where c_{st} = start solution count, c_s = sample solution count, c_{bk} = background count

2.2.2. Interference Experiments

For the interference experiments varying quantities of inactive components were added. The above experiment was therefore repeated in the presence of 50ppm ruthenium (as ruthenium nitrosyl nitrate), or 25ppm antimony (as potassium antimonate) or 50ppm strontium (as strontium nitrate). Finally a more accurate simulant was produced by dissolving ferric nitrate, sodium dihydrogen phosphate and uranyl nitrate in 260g/dm^3 sodium nitrate to give a total volume of 250cm^3 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. At this point the technetium was added as ammonium pertechnetate and 3.83μl of TBP - this solution is termed "full simulant" in the text and illustrations below.

Figure 4. Cross-section of Kilner cell.

The variation in count rate and DF with time is illustrated·in figure 5.

From the data supplied in these figures (5&6) it can be seen that the presence of the strontium and antimony did not alter the rate of technetium removal. When ruthenium or "full simulant" were present, however, the initial rate of technetium removal was reduced - i.e. there was an induction period before the removal of the target species. For the full simulant, it is unclear as to the cause of the induction period since the electroactive components (mainly uranyl and ferric) were removed during the precipitation and filtration. The induction period caused by the ruthenium is more straightforward to explain. The ruthenium nitrosyl nitrate present in the mixture is oxidised to ruthenium tetroxide on the anode and then irreversibly reduced to ruthenium dioxide on the cathode.

$$RuNO^{3+} \xrightarrow{\text{oxidation}} RuO_4 \xrightarrow{\text{reduction}} (RuO_2.H_2O)_n(RuO_4)ads.$$
$$\xrightarrow{\text{reduction}} (RuO_2.H_2O)_{n+1}$$

This can be confirmed by noting that a black precipitate was formed during the experiment, and by considering the analytical data supplied in table 2.

Figure 5. Variation of background corrected count with time for solutions as described in text.
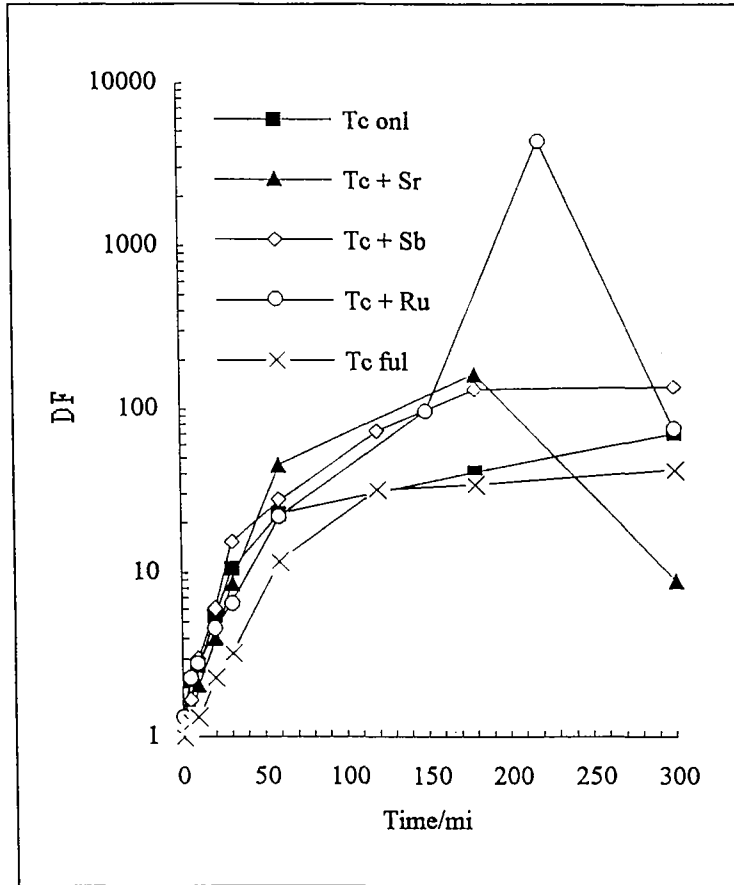
Figure 6. Variation Of DF with Treatment Time.

Table 2. Variation in inactive component during interference experiments.

Time/mins	Ru/ppm	Sb/ppm	Sr/ppm
0	57.5	27.5	50
10	55	27.5	50
30	25	20.75	50
60	22.5	18.25	50
180	<2.5	22.75	50
300	<2.5	25	50

Under the experimental conditions studied, the ruthenium was removed before technetium deposition. There was some evidence that antimony is removed from nitrate solution but clearly no deposition of strontium occurred during these runs.

The level of ruthenium in the genuine waste is approximately 3ppm - the experiment described above was performed at about 50ppm. To establish that the presence of the ruthenium would not detract from the technetium removal process the experiment was repeated using 3ppm Ru. The results (in terms of technetium removal) were almost identical to those obtained without ruthenium. Under the conditions studied in this experiment, there was no noticeable darkening of the solution with ruthenium dioxide -

although from previous work in this area a decrease in ruthenium content to less than 0.1ppm (a DF of about 30) would be expected.

2.2.3. Loading and Corrosion Experiments.

The aims of this series of experiments were to:

(i)   Establish whether film growth continued over longer time periods.
(ii)   Determine whether the active oxide was stable under the solution conditions prevalent in the cell.

2.2.3.1. Loading Experiment.

A film of TcO_2 with a thickness of $1\mu m$ and a density of $4g/cm^3$ will possess a total activity density of approximately $290kBq/cm^2$. A stainless steel wire electrode was manufactured with an exposed area of $3.85 \times 10^{-3}cm^2$. At the above loading, this would correspond to approximately 1100Bq on the exposed surface. In our simulants our solutions contained only $50Bq/cm^3$ - a total of 12500Bq. On an area pro-rata basis, 1100Bq of activity would be lost from the solution over a period of 8 months - too long for the intended study. To reduce the time involved the solution concentration was increased to $1kBq/cm^3$. Over a six day period, the solution activity decreased by approximately 27% - a total activity loss of 67.6kBq. This would correspond to a film thickness of $60\mu m$. Examination under an optical microscope did not identify a film of this thickness. The conclusion was that some absorption may have occurred on the glassware over this extended period. After considering these results, it was decided to leave the loading capacity experiments until the real runs at Sellafield since the technetium concentration in these streams is roughly 200 times higher than in the solution studied at Harwell.

2.2.3.2. Corrosion Experiments.

A solution of "full simulant" was prepared and a sample taken for counting. The electrode was then loaded for 270 minutes and the power switched off. After 3000 minutes nearly all the activity was present in the solution, i.e. the technetium film had dissolved. The experiment was repeated under the following "power off" conditions.

(i)   Power off with argon (deoxygenated to prevent reoxidation)
(ii)   Power off, electrode held at -0.4V vs. SCE.
(iii) Power off, electrode held at -0.6V vs SCE.
(iv)   Power off, electrode held at -0.675V vs SCE.

The variation of solution activity with time during these experiments is illustrated in figure 7.
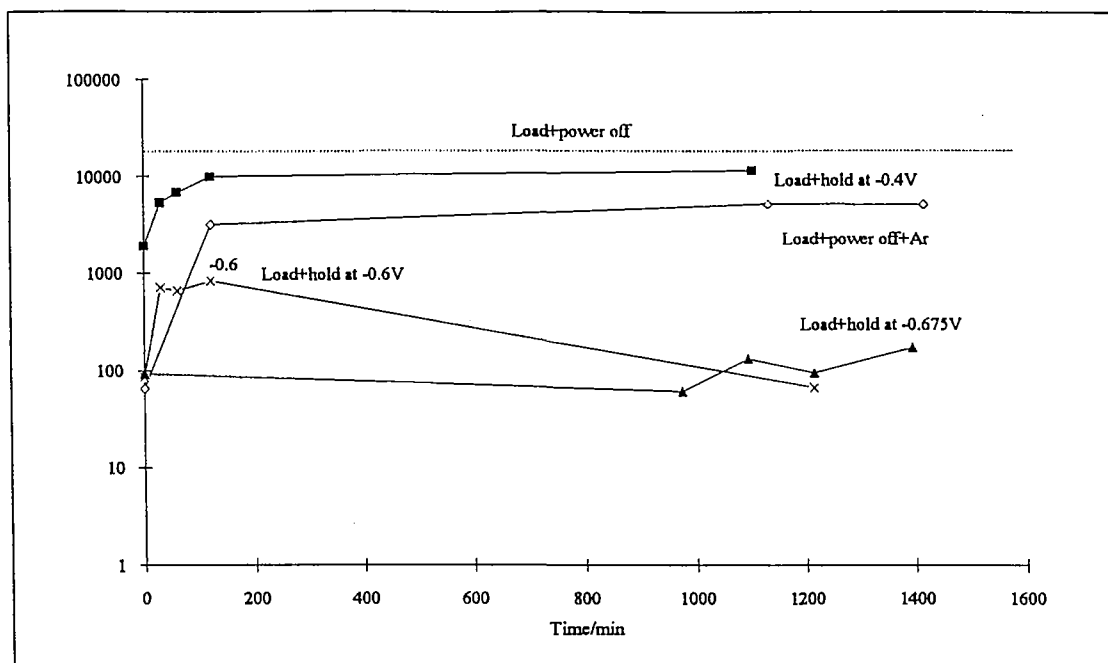
Figure 7. Variation in solution activity (in counts per hour) with time during power off experiments described in text above.

By comparing experiments (ii) and (iii) we can see that the presence of oxygen does cause some corrosion problems. However, it would appear that the use of cathodic protection process (at potentials less than or equal to -0.675V) are adequate for the prevention of redissolution of the active film. The exact mechanism for the corrosion process is uncertain. The most important reaction may be between the electrolyte and the oxide film rather than reoxidation by the dissolved oxygen since bubbling with argon only slowed the redissolution process.

2.4. Experiments on Genuine EARP Waste.

Having established that it was possible to remove technetium from simulant wastes it was decided to continue with the treatment of genuine EARP treatment MAC waste. The work was carried out by Drs. F. E. Raymont (BNFL) and P. A. Fletcher (AEA) at Sellafield using a batch cell similar to that illustrated in figure 4. A detailed description of the experiments performed and the results obtained is supplied in Appendix 1. In summary:

Experiment 1 - Commissioning experiment

A stream containing technetium in nitrate was treated with activity reduced from 82.6 to $0.932Bq/cm^3$ within 60 minutes, a DF of greater than 88.

Experiment 2 - Commissioning experiment

A stream containing technetium in nitrate was treated with activity reduced from 92 to $0.851Bq/cm^3$ within 60 minutes, a DF of greater than 108.

Experiment 3 - Run on genuine waste.

A permeate prepared by treating actual M.A. concentrate in the EARP miniature active pilot plant was initially diluted by a factor of 10 and then treated electrolytically. The technetium activity of the solution fell from 19,300 to 10.9 Bq/cm^3 over a period of 5 hours. This result represents a decontamination factor in excess of 1700. The time required for a DF of 10 was approximately 45 minutes. During the treatment period a ruthenium DF of 3 was observed. It should be noted that the samples were not filtered and that filtration might have resulted in an increase in both the technetium and ruthenium DFs.

Experiment 4 - Run on genuine waste.

A permeate prepared as above was initially diluted by a factor of 10 and then treated electrolytically using the same electrode as the previous experiment (i.e. a technetium loaded electrode). The technetium activity of the solution fell from 22,100 to 33.5 Bq/cm^3 over a period of 5 hours. This result represents a decontamination factor in excess of 650. The time required for a DF of 10 was approximately 60 minutes. During the treatment period a ruthenium DF of 1.5 was observed. Again it should be noted that the samples were not filtered and that filtration might have resulted in an increase in both the technetium and ruthenium DFs.

Experiment 5 - Corrosion Experiment.

This experiment was not part of the prescribed programme and was performed by Dr. F.E. Raymont (BNFL). As before, these results are provided in the Appendix.

3. CONCLUSIONS AND FUTURE WORK.

This part of the programme has examined the potential interference of a number of species on the technetium deposition process and the potential problems that may occur during long term storage of the technetium coated electrodes. The following represents a summary of the results obtained during the programme.

3.1. Interference experiments:

Sr	No noticeable effect on Tc removal - No change in Sr concentration.
Sb	No noticeable effect on Tc removal - No systematic change in Sb concentration.
Ru	For high levels of Ru; Ru removed before Tc (Ru DF >23) then Tc removal. At realistic levels of Ru, the induction period is so short as to be inconsequential.
Mixture	Short induction period, however Tc removal to DFs >30 still obtained.

It should be noted that the target DF for this process is between 5 and 10.

3.2. Redissolution experiments:

Power off	Tc coating redissolves slowly.
Cathodic protection -0.4V	Tc coating redissolves slowly.
Ar saturation (deO$_2$)	Tc coating redissolves slowly.
Cathodic protection -0.6V	Tc coating redissolves more slowly than at -0.4V.
Cathodic protection -0.675V	Very slow, almost inhibited redissolution.

3.3. Genuine Waste:

Treatment of permeates prepared from actual MA concentrate gave excellent results. Technetium DFs of greater than 1700 and 650 were observed during sequential experiments. The ruthenium DFs were more disappointing - this may be improved by use of a suitable post filtration treatment.

In conclusion we can observe that the electrolytic process was successful in treating both simulant and genuine permeates. The target DF of ten was easily achieved - and always exceeded by at least one order of magnitude. There was a small but significant decrease in the amount of ruthenium - this decontamination may be improved by post filtration. There was no systematic removal of either antimony or caesium. As regards to corrosion of the deposited technetium upon power interruption - this does represent a potential problem arising from the mild oxidising nature of the waste. However, two solutions have been proposed and tested successfully on the simulant streams. These involve either:

(i)   Emptying the cell during periods of non operations.

(ii)   Biasing the cell at approximately -0.7V vs SCE (i.e. cathodic protection).

It was not possible to test either of these options on the genuine waste.

3.4. Future Work

The programme has proved to be largely successful - achieving the DF goals outlined at the start of the work. There is still some work required before proceeding to even pilot scale operations. This work should include:

(i)   Development and testing of a suitable flow cell to establish performance data and scale up factors*.

(ii)   Examination of electrode materials - anode and cathode - to minimise cost*.

(iii)   Confirmation of the validity of the corrosion prevention options*.

(iv)   To establish the maximum loading capacity of the system - given fixed performance targets**.

(iv)   Disposal route for the technetium plated cells - grouting mixtures**.

The work breakdown for this programme is divided into effort from AEA* and BNFL** as indicated above.

4. HAZARD ASSESSMENT REPORT.

Guideword	Fault	Consequences	Action
Contamination.	Leakage of process liquids.	Hazard to operators.	1. Commission inactively 2. Contain the plant in a containment vessel of suitable size. 3. Provide level sensors in the containment vessel to cut power to the pump in the event of the liquid level rising in the tray. 4. Filter any gas purges in order to prevent leakage via aerosols. 5. Care to be exercised during final grouting.
External Radiation	High radiation from cell.	High dose to operator.	1. Monitor radiation levels regularly 2. Use appropriate shielding based upon calculations of the loading of the cell with known nuclides.
Explosion	Hydrogen/Oxygen ignition at point of gas release to the environment	Injury to operator Damage to plant	1. Purge gas venting system with air to reduce hydrogen concentration to below 20% of the explosive limit.
Electrical	None - Installation by qualified personnel - low voltage system.	None	None
Effluents.	Splashing of effluents	Injury to operator and damage to cell.	1. Wear protective clothing when performing operations that may lead to contact with effluent. Treat contamination as for contact with untreated waste. 2. Construction to be waste compatible.
Loss of service	Mains failure (electricity)	Process will fail safe. Liquid flow stops. Electrochemical processes, gas evolution stops	1. Operator will restart when power available 2. Design cell such that power failure results in return of cell contents to start of treatment cycle and prevents entry of contaminated waste into the cells. 3. Automatic drain from cell. 4. Monitor treated waste since some product corrosion may occur.
Process maloperation	1. Power supply unit failure 2. Pump failure 3. Liquid leaks from system 4. Failure of air purge	Electrochemical process stops. Flow of feed stops. Possible contamination. Hydrogen gas concentration may increase above the lower explosive limit in air at the point of release.	1. As for power failure above. 2. Correct fault and restart 3. Arrange sensor/cut-out system to operate as for power failure, this is not urgent since over treatment of solution does not represent a risk. 4. Correct fault and restart. 5. As for contamination. 6. Arrange a gas flow sensor/cut-out system to cut electrical power from the system and then operate as for an electrical failure.
Maintenance	Failure of pumps	Leakage and contamination	1. Change pumps according to manufacturers instructions.
Loss of containment	Leakage of liquid	Contamination	1. Check the condition of all perishable tubing before each run or test. 2. Check tightness of cell bolts.

Dr. F.E. Rayment, Effluent Treatment Research Group, Sellafield Technical Department, Sellafield.

Introduction

A few years ago the Enhanced Actinide Removal Plant (EARP) was developed at ·BNFL, Sellafield, for the removal of mainly α activity from the bulk liquid effluent streams on site, using a ferric floc precipitation technique. In addition to the removal of the vast majority of a activity, extra precipitants are added at much lower levels to the delay storage evaporator concentrate, to give enhanced β/γ removal from these streams. Typical aqueous waste compositions can be seen in table A.1.

Although much of the activity is removed from the concentrate, there is still a small amount of soft β radiation present in the permeate after flocculation due to the presence of the ^{99}Tc radionuclide. A project was therefore set up to examine various electrochemical methods for ^{99}Tc removal from the EARP permeate stream. Among the many electrochemical methods initially examined were direct electrochemical reduction of pertechnetate, electrochemical ion exchange, direct removal by seeded ultrafiltration, and reduction of pertechnetate to insoluble TcO_2 or base metal. Of all the techniques studied direct electrochemical reduction was judged to be the most promising and therefore an experimental programme was initiated jointly by BNFL and HMIP for scoping trials to be carried out on this technique.

A number of initial experiments were carried out by AEA Technology, Harwell (Applied Electrochemistry Section) using a simulate stream which contained $27g/dm^3$ sodium nitrate at pH 10, which is consistent with the concentration of nitrate within the EARP permeate. To this simulate was added a variety of metal cations or anions which could be found within the EARP permeate, and may interfere with the reduction of Tc (VII) to Tc (IV).

These initial experiments with simulate indicated that a small amount of ruthenium may be plated out on the electrode, as the dioxide, in addition to the plating out of TcO_2. After this initial experimentation the cell was brought to BNFL, Sellafield, to carry out some active tests on medium active concentrate liquor treated in the laboratory in the EARP miniature active pilot plant, in order to verify that technetium could be plated out as the dioxide on a stainless steel cathode, in addition to studying the potential interference by any other ions present in the liquor.

Experimental

The reduction of Tc (VII) in alkaline solutions generally follows the sequence:

$$Tc\ (VII) \rightarrow Tc\ (V) \rightarrow Tc\ (IV) \rightarrow Tc\ (0)$$
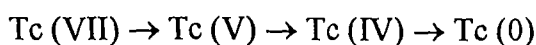
The Tc (VII) and (V) are soluble and Tc (IV) and (0) are insoluble in aqueous nitric acid under normal conditions of temperature and pressure and hence when Tc (VII) is reduced electrochemically, a solid black deposit of TcO_2 [Tc (IV)] is produced on the electrode. The bare technetium metal would only be produced under more reducing conditions.

The following experiments used a stainless steel cathode to reduce TcO_4^- to TcO_2 (Tc IV) in basic solution which was electrodeposited as a noticeable grey deposit on the electrode.

The electrodeposition was carried out using a Kilner cell, which consisted of a 500cm³ Kilner jar, into which was placed two concentric cylindrical electrodes. A Luggin capillary was held against the inner surface of the outside working electrode. A Standard Calomel Electrode (S.C.E) was contained in a vessel at the other end of the Luggin capillary in order to keep the cell at a constant potential which was +1.0V with respect to the S.C.E. The anode used was platinised titanium expanded mesh, 1mm thick, due to its radiolytic stability whereas the cathode was type 304 stainless steel (100 mesh) which had a 23 cm circumference.

The cell was initially commissioned using a simulate stream which consisted of a 2.6M solution of $NaNO_3$ buffered to a pH of 10.4 with NaOH and to this was added 100 Bq/cm³ TcO_4^-. A total amount of 250 cm³ of the solution was added to the Kilner cell and the potential was kept at a constant of 1V with respect to the S.C.E. and allowed to run, with constant stirring, for a total time of 60 minutes. Samples were removed at regular intervals, using a syringe, from the middle of the cell. This experiment was carried out in duplicate and the results obtained can be seen in Tables A.2. and A.3. and Figures A.2. and A.3.

The next stage in the experimental work was to use the same technique to electrodeposit ^{99}Tc from the EARP MAC permeate produced in the laboratory from a plant sample of the MA concentrate by the procedure employed in EARP. This permeate (250 cm³) was added to the Kilner cell and the cell was allowed to run for a total time of 5 hours at a potential of IV with respect to the S.C.E. Samples were taken at regular intervals throughout using a calibrated syringe. These samples were then analysed for ^{99}Tc using the technique of liquid scintillation counting and a scan was undertaken to examine for the presence of any β/γ emitters. This work was carried out once again in duplicate and the results obtained can be seen in tabulated form in the appendix (Tables A.4. - A.9.). Figures A.6. and A.7. indicate the Decontamination Factors (DFs) obtained for any other radionuclides present within the permeate. It is worth mentioning that the second set of experiments (run 4) were undertaken with a cathode which had already TcO_2 deposits on it from the previous run and therefore the DFs obtained with respect to time were not as high.

Once these experiments were completed, the current was switched off and the technetium loaded cathode was immersed into a fresh solution of EARP MAC permeate (250 cm³). Samples were taken from the solution at regular intervals to determine whether the technetium would redissolve in solution when the applied

current was switched off. The results obtained can be seen in the appendix in table A.10.

Results and Discussion

It can be seen from figures A.2. and A.3. that the pertechnetate anion [Tc(VII)] can be removed quite readily from solution using electrochemical methods. The TcO_4^- is reduced to [Tc(IV)] in the form of the dioxide. Moreover, a large amount of the technetium dioxide is deposited on the cathode giving DFs in the region of 100 after a total time of 60 minutes batch cell operation. After initial loading of Tc on the electrode from the 3rd run, the 4th run produced slightly lower DFs with respect to time. This is most probably due to the additional deposit of TcO_2 an the electrode surface, which in turn would make the electrode slightly less efficient due to the higher overpotentials which would be generated within the cell. This increase in overpotential is due to the less conducting nature of the oxide which is now contained on the electrode surface. The technetium dioxide is readily seen on the electrode surface as a dull grey deposit which appeared on the cathode after approximately 30 minutes of operation. This deposit was tested for activity using a hand held RO2 (used for monitoring, β/γ radiation) and proved to be giving off large amounts of β radiation (approximately 2.5 mSv/h).

Any other radionuclides removed from the permeate in comparison with the amount of ^{99}Tc removed were negligible (Figures A.6. and A.7.). The pH of the solution did not fluctuate very much during cell operation and the current remained constant throughout after dropping to an initial equilibrium value.

Once the current is switched off the technetium dioxide on the loaded electrode slowly dissolves back into solution as the pertechnetate anion. This occurs at a slow rate probably due to the amount of pertechnetate already contained within the EARP MAC permeate.

Further work

Further work is needed for methods of retaining the technetium on the electrode when there is no electrical potential being supplied to the system. In addition to this, further work is required to devise a flow cell which will give high enough DFs when lower contact times and much faster flow rates apply, as in a large scale plant. Other types of anode will need to be examined as platinised titanium is too expensive a material for any commercial process to run economically. One type of material which may be worth examining is Dimensionally Stable Anodes (DSA) which consist of oxide layers of Ti and similar metals and are extremely radiolytically stable. Methods of disposal of the radioactive cell would also be required. One likely method is encapsulation of the Tc loaded electrode using typical BNFL grouting techniques.

Much more research is therefore required into this method of treatment, before this could be of use as a large scale process.

Conclusion

The initial scoping trials show that this procedure may have potential for the removal of ^{99}Tc from EARP MAC permeate. However, a considerable amount of further research and development work would be required to determine whether or not this could be a viable process. Indication of the areas of further work required are given in the text.

Table A.1. Summary of Composition Of EARP stream.

Volume 1800m³/y (2-4m³/h batch) Permeate Acidity pH10.5			
Major Inactive Species	Concentration		
HNO(M)	7.5 - 8.3		
Na(g/dm³)	3.0 - 7.0		
Fe(g/dm³)	1.6 - 4.6		
TBP(ppm)	5.0 - 60		
Significant Active Species	Activity/(Bq/cm³)	Permeate/(Bq/cm³)	*DF
^{106}Ru	50000	1250	40
^{144}Ce	10000	40	227
^{90}Sr	70000	23000	3
^{95}Zr	200	13	15
^{95}Nb	1000	6.6	152
^{137}Cs	100000	2500	40
^{99}Tc	200000	200000	1
Pu alpha	10000	2	5000
^{251}Am	8000	4.6	1739
^{237}Np	1000	0.3	3333
^{60}Co	100	6.4	16
^{134}Cs	5000	125	40

*The DFs are calculated by dividing the feed activity by the permeate activity. The permeate is the aqueous liquor left after flocculation of the feed.

Table A.2.

Sample	time/mins	I/mA	Activity/(Bq/cm³)	Error	DF
FERTC1A	0	160	82.6	(±) 2.85	0
FERTC1B	30	90	5.38	(±) 0.95	15
FERTC1C	60	103	0.932	(±) 0.72	89

Table A.3.

Sample	time/mins	I/mA	Activity/(Bq/cm³)	Error	DF
FERTC2A	0	220	92	(±) 3	0
FERTC2B	30	120	2.84	(±) 0.83	32
FERTC2C	60	105	0.851	(±) 0.71	108

Table A.4.

Sample	time/mins	I/mA	Activity/(Bq/cm³)	Error	DF
FERTC3A	0	100	19300	(±) 1380	0
FERTC3B	15	61	10000	(±) 714	1.9
FERTC3C	30	54	2750	(±) 19.7	7
FERTC3D	60	55	158	(±) 12.1	122
FERTC3E	120	59	25.2	(±) 2.63	765
FERTC3F	180	60	15	(±) 1.96	1286
FERTC3G	240	59	11.4	(±) 1.74	1693
FERTC3H	300	58	10.9	(±) 1.72	1770

Table A.5.

Sample	time/mins	I/mA	Activity/(Bq/cm³)	Error	DF
FERTC4A	0	120	22100	(±) 1490	0
FERTC4B	15	67	17800	(±) 1200	1.24
FERTC4C	30	66	11000	(±) 743	2
FERTC4D	60	63	2040	(±) 138	11
FERTC4E	120	67	118	(±) 8.74	187
FERTC4F	180	66	75.5	(±) 5.9	293
FERTC4G	240	66	52.1	(±) 4.31	424
FERTC4H	300	64	33.5	(±) 3.08	660

Table A.6.

Sample	time /mins	^{99}Tc /(Bq/cm³)	^{106}Ru /(Bq/cm³)	^{125}Sb /(Bq/cm³)	^{137}Cs /(Bq/cm³)
FERTC3A	0	19300	500	60.7	11.9
FERTC3B	15	10000	513	59.2	18.5
FERTC3C	30	2750	513	53.1	16.5
FERTC3D	60	158	418	54.1	14.6
FERTC3E	120	25.2	13	55.0	11.3
FERTC3F	180	15	233	53.2	8.97
FERTC3G	240	11.4	239	59.2	13.4
FERTC3H	300	10.9	186	65.8	14.8

Table A.7.

Sample	time/mins	DF ^{99}Tc	DF ^{106}Ru	DF ^{125}Sb	DF ^{137}Cs
FERTC3A	0	1	1	1	1
FERTC3B	15	2	1	1	1
FERTC3C	30	7	1	1	1
FERTC3D	60	122	1	1	1
FERTC3E	120	766	38	1	1
FERTC3F	180	1287	2	1	1
FERTC3G	240	1693	2	1	1
FERTC3H	300	1771	3	1	1

Table A.8.

Sample	time /mins	^{99}Tc /(Bq/cm³)	^{106}Ru /(Bq/cm³)	^{125}Sb /(Bq/cm³)	^{137}Cs /(Bq/cm³)
FERTC4A	0	22100	482	61.6	17.8
FERTC4B	15	17800	483	61.1	14.6
FERTC4C	30	1100	516	53.9	17.2
FERTC4D	60	2040	485	47.4	17.3
FERTC4E	120	118	423	58.7	22.2
FERTC4F	180	75.5	330	70	22.1
FERTC4G	240	52.1	351	59.1	24.2
FERTC4H	300	33.5	291	60.8	24.4

Table A.9.

Sample	time/mins	DF ^{99}Tc	DF ^{106}Ru	DF ^{125}Sb	DF ^{137}Cs
FERTC4A	0	1	1	1	1
FERTC4B	15	1	1	1	1
FERTC4C	30	20	1	1	1
FERTC4D	60	11	1	1	1
FERTC4E	120	187	1	1	1
FERTC4F	180	293	1	1	1
FERTC4G	240	424	1	1	1
FERTC4H	300	660	2	1	1

Table A.10.

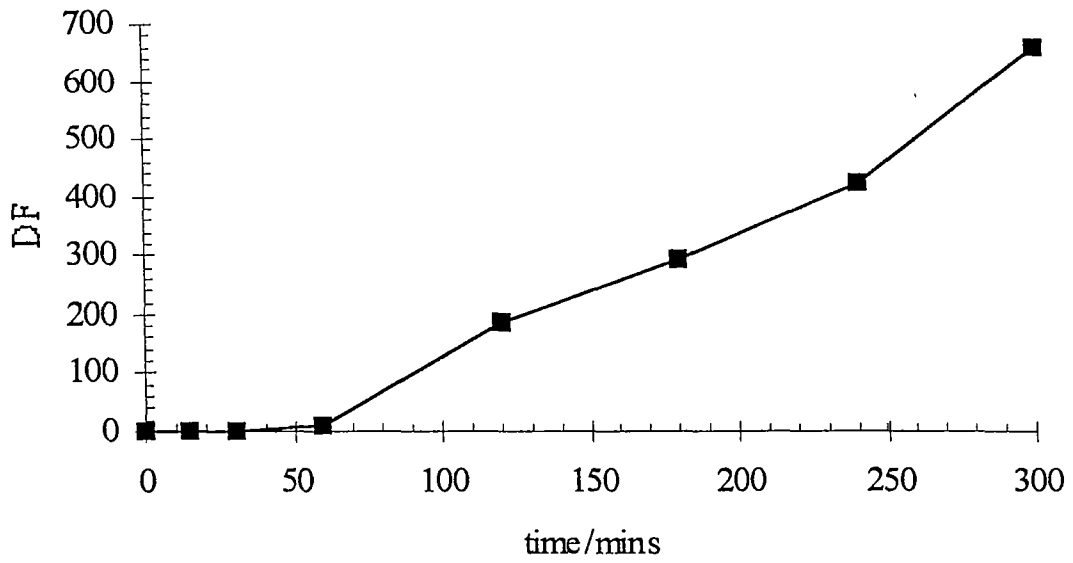| time /mins	^{99}Tc /(Bq/cm^3)	^{106}Ru /(Bq/cm^3)	^{125}Sb /(Bq/cm^3)	^{137}Cs /(Bq/cm^3)	^{134}Cs /(Bq/cm^3)
0	29200	466	55.6	30.0	1.49
30	28100	479	56.1	34.4	1.19
60	30500	490	50.9	35.5	1.74
120	32400	508	56.8	36.4	3.0
180	31900	526	58.1	35.8	2.51
240	31700	510	55.2	38.2	2.12
300	32500	552	58.6	37.4	1.96
1440	34000	509	53.7	30.6	1.55
2880	42400	602	59.8	28.7	2.40
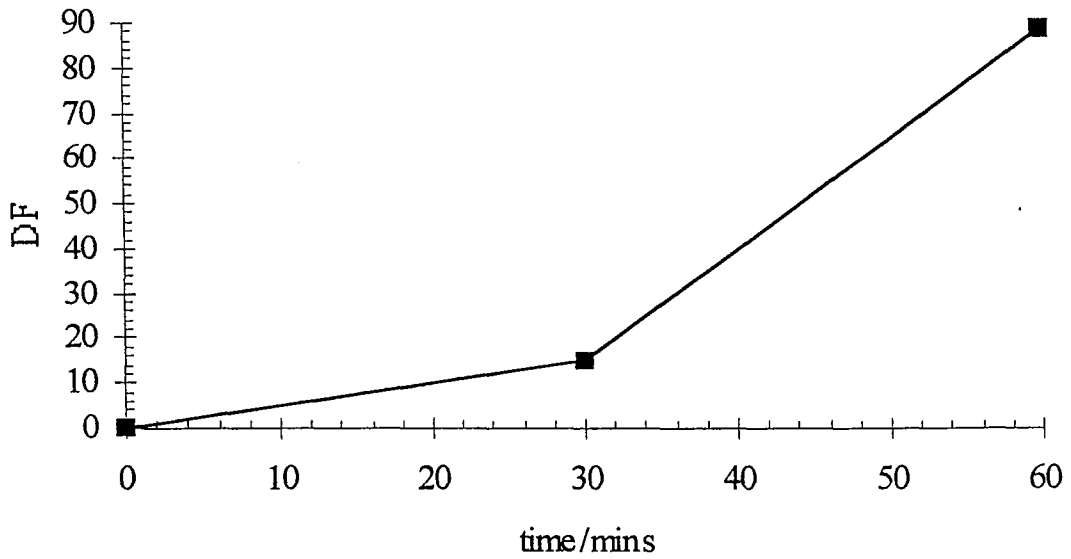
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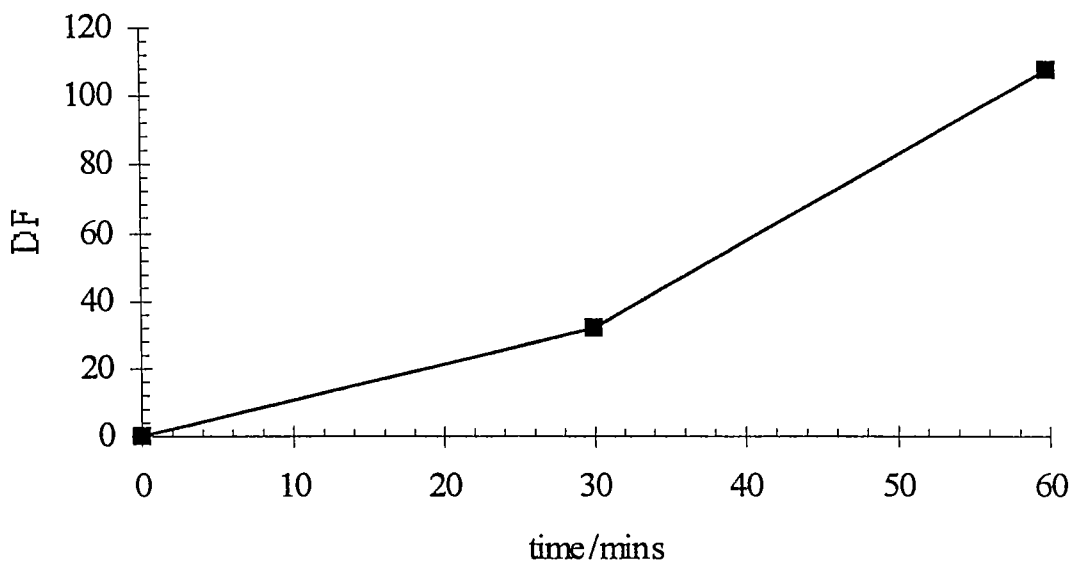
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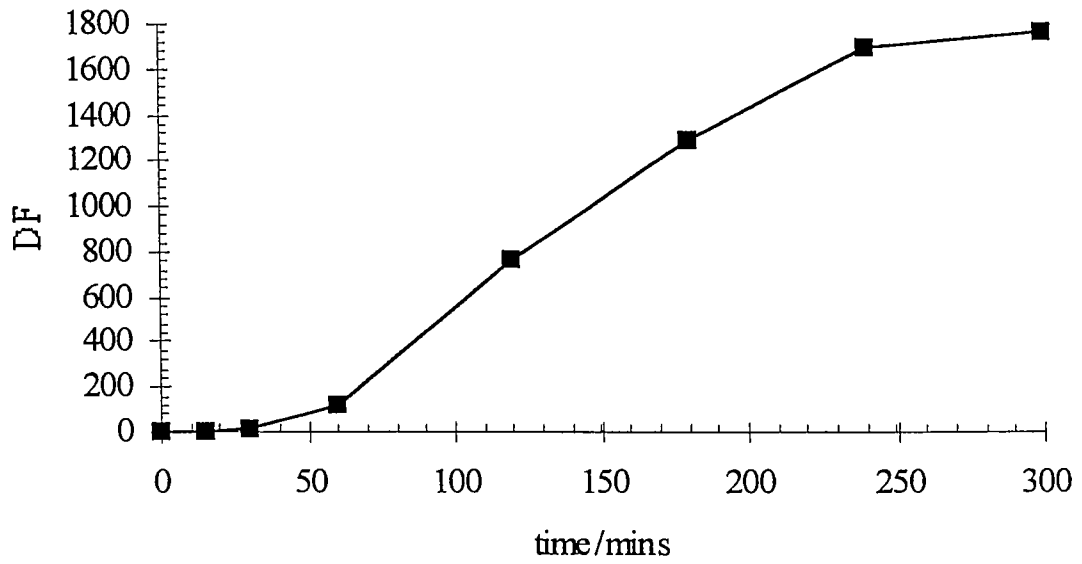
Figure A.4.

Figure A.5.

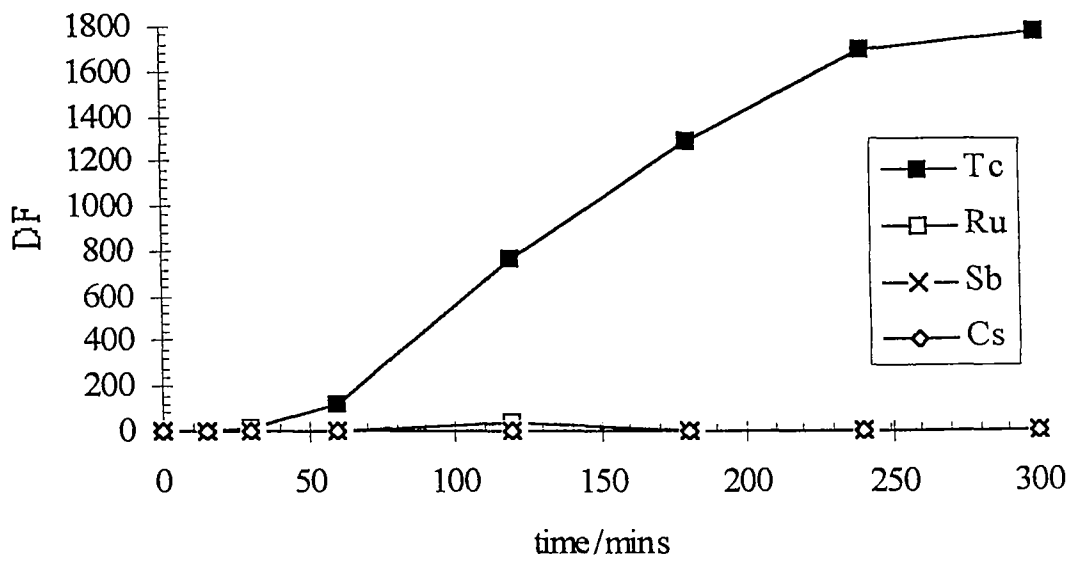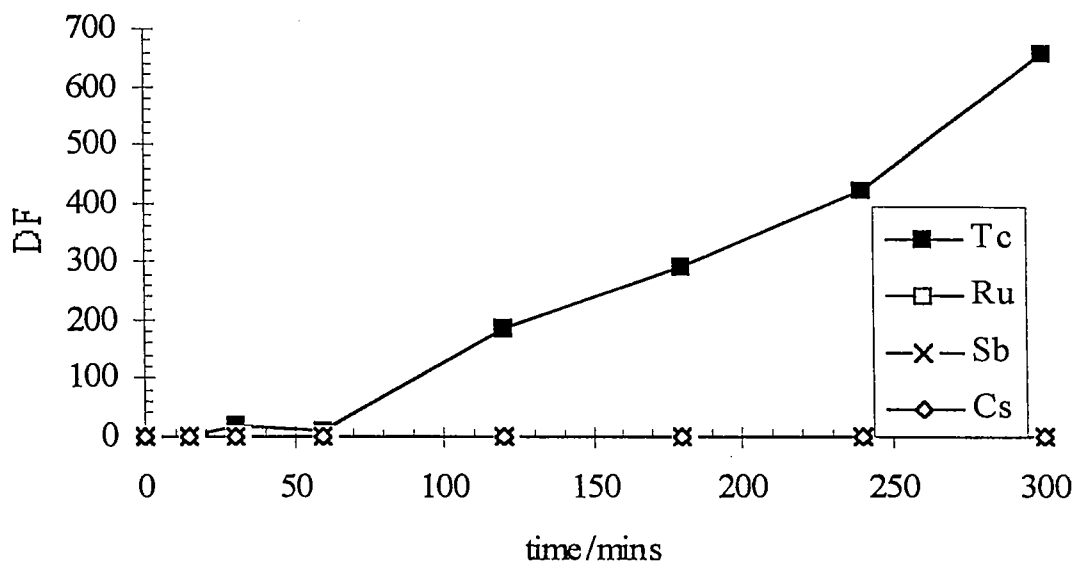

Figure A.6.

Figure A.7.