DISPOSAL OF ORGANIC ION EXCHANGE RESINS CONTAMINATED WITH TECHNETIUM 99

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ABSTRACT

Experiments have been carried out to determine suitable anion exchange resins for the uptake of technetium from aqueous solutions. These experiments were carried out in three stages reducing the number of resins studied after each stage. Stage 1 was a simple screening exercise using equilibrium distribution coefficients. Stage 2 was the examination of thermal, radiation and chemical stability followed by an examination of diffusion, column and isotherm characteristics. Stage 3 was the selection of a suitable disposal method and matrix followed by the examination of leaching characteristics. This paper presents the results for Stage 3 of this work.

INTRODUCTION

Technetium 99 is a long lived isotope (2.12E + 5 year half life), mainly produced as a byproduct of fission in nuclear reactors, but also used in hospitals for radioimmunoassay and scanning. Due to its potential radiotoxicity in the long-term after release from a repository, technetium 99 has been identified (1) as one of the isotopes of concern in post-closure safety considerations.

This paper identifies the various treatment options available for contaminated ion exchange resins and details the results of experiments carried out on the leaching of technetium from the matrix selected for further study.

DISPOSAL OF TECHNETIUM BEARING ION-EXCHANGE RESINS

The policy for the disposal of organic ion exchange resins has not yet been decided upon in the United Kingdom. Various options are available and these were considered in light of specific problems relating to technetium.

Various destructive techniques have been used, or are under development, for the treatment of spent ion exchange resins. These can be considered to comprise incineration, wet oxidation or electrochemical oxidation.

Incineration (2) at various temperatures and pressures, with and without the use of catalysts, results in the destruction of organics with large decreases in mass and volume but, due to volatilization of many radionuclides (for Tc-99 between 10 - 60% can be lost), results in costly process control and off gas treatment.

Wet oxidation processes such as acid digestion using concentrated sulphuric acid with a few percent of nitric acid or sulphuric acid/hydrogen peroxide (3) are feasible. These process are still in the development stage. Additional processes are WINWOX (4) which has been developed by AEA Technology Winfrith which uses hydrogen peroxide and a transition metal catalyst and AEA Technologies Dounreay's electrochemical oxidation process which uses anodically generated silver (II) as an oxidant.

Other techniques that have been used are drying followed by compaction (50 - 75% volume reduction depending on compaction pressure) (5) or the use of MOSAIK containers (6) for direct disposal of ion exchange resins.

Encapsulation is the simplest method and involves the incorporation of the resin in a suitable matrix. The matrix forms a barrier to prevent or retard the leaching of radionuclides from a repository. Various matrix forms are available these being cement, polymers, bitumen and vitrification.

Cementation is a well proven technique and is proposed, or is in operation for many other types of waste. The encapsulated product is non flammable, has the potential for good thermal, chemical and physical stability, and produces an alkaline environment which inhibits the solubilities of many of the long lived radionuclides. Pulverized Fly Ash and Blast Furnace Slag are used in varying proportions depending on applications it is has been proposed that the use of polymer additives could enhance the matrix stability and reduce leaching of radionuclides.

Polymers used (7) in the treatment of ion exchange resins such as polyester and epoxy resins are compatible with the resin but generally considered more expensive and more complex than other processes and increase the amount of organics entering a repository. The introduction of additional organics is undesirable due to the increased solubilities of significant radionuclides that can be caused by organic degradation products.

Bitumenization, like the polymer process, is also a relatively complex process but has drawbacks of flammability and the final product is not of good stability.

For vitrification, dewatered resin is calcined with a glass frit to form a uniformly powdery mixture which is then fused to form glass. However loss of technetium (40 - 60%) occurs (8, 9) at the high temperatures used which makes this process unsuitable for this application and, like incineration, off-gas treatment is required.

SELECTION OF CONDITIONING PROCESS FOR FURTHER EXAMINATION

From the examination of the techniques for conditioning of ion exchange resins cementation is by far the simplest process and the product has good stability (thermal, chemical and physical).

The potential problem with the use of cement as a matrix for ion exchange resins is the stability of the product if the resins within the matrix swell due to the ingress of water. A

solution to this, considered in this work, was the use of polymer additives to enhance the stability of the matrix and to reduce leaching of radionuclides.

PRELIMINARY EXPERIMENTAL WORK

Preliminary experimental work (16) was carried out in two stages.

Stage 1: - Initial screening of commercially available resins.

Twenty two anion exchange resins were initially examined and screened using simple equilibrium distribution coefficient experiments for pertechnate in nitric acid (1-8 M), pond water and evaporator concentrate.

Stage 2: - Examination of resin chemical, radiation and thermal stabilities, followed by determination of diffusion, column and isotherm characteristics.

Radiation stability experiments were carried out using a Colbalt 60 source and irradiating 6 resins in pond water and evaporator concentrate for doses 10^4, 10^6 and 10^8 rads. Performance was measured by determination of distribution coefficients.

Thermal stability experiments were carried out on 6 resins for temperatures of 100°C and 200°C for 1 week with performance measured by determination of distribution coefficients.

Chemical stability experiments were carried out for 6 resins in 1-8M nitric acid and 1-8M sodium hydroxide solutions for 2 months with performance measured by the determination of distribution coefficients.

From these experiments two resins were identified as having optimum stability and column characteristics; low temperature diffusion coefficients and isotherms were determined.

LEACHING EXPERIMENTS

This paper presents results of leaching experiments (16) on ion exchange resins identified as suitable for the removal of technetium from various aqueous liquors, and encapsulated in polymer cements.

Two resins were identified in the preliminary experimental work as particular suitable for use in the removal of technetium from aqueous liquors. Thermax Tulison A27 MP (macroporous type resin) and polyvinyl pyridine resin (Reilly Tan and Chemicals) were encapsulated in four polymer matrices (Liquid Plastics, Preston) which are given in Table I. Additional samples were encapsulated in BFS:OPC (9:1) for comparison.

Leaching experiments were carried out using the IAEA standard leach test (10, 11, 12, 13) which gives a simulation of a range of water flow regimes controlled by exchange of leachant solution.

Two simulated groundwater leachants were used. These are outlined in Table II.

The leach rates are expressed as a plot of the cumulative fractions of radioactivity leached from the species as a function of the leach time.

$$\sum \frac{A_n}{A_o} \mid \frac{F}{V} \textit{versus} \sum \sqrt{t_n}$$

where

A_n = radioactivity leached during the leachant renewal period (nominal units)

A_o = radioactivity initially present in the specimen (nominal units)

F = exposed surface area of specimen (cm^2)

V = volume of specimen (cm^3)

t_n = duration (days) of leachant renewal period

Extrapolation of leach test data to a disposal program was also considered by calculation of the diffusion coefficient of the leaching of the radionuclide from the matrix. Godbee et al (16) have shown that Fick's diffusion equations can be used to describe (some cases only approximately) the leaching process. However a simple Fickian-type system was not considered suitable to describe the leaching of radionuclides from a cement matrix containing ion exchange resins. Therefore the Carman-Haul equation for cylinder geometry was applied to the experimental results to determine a more accurate value (if diffusion controlled) than the leach factor. This method assumed that the diffusion process was dependant on diffusion out of the resin beads and not diffusion from the surfaces of the waste form (film diffusion). This is likely to be the case during the initial period of leaching and the major factor for

TABLE I

Flexcrete Polymer Cements

Sample	Mix Ratio A:B	Polymer content	Polymer type	Micro-Silicon content
FCR81	1:3.8	Very high	Styrene - Acrylic (soft)	High
FCR854	1:6	Average	Styrene - Acrylic (hard)	High
FCR864	1:6	Below average	Methylmethacrylate	Nil
FCR853	1:7	Average	Styrene - Acrylic (hard)	Low

TABLE II

Composition of Simulated Groundwater

Compound used empirical formula	M. Wt.	Concentration meq l^{-1}	mmol required 0.5 l	Wt. required gl^{-1}
Ground water C				
$NaHCO_3$	84.01	11.00	5.50	0.92
$Ca(NO_3)_2.4H_2O$	236.1	1.00	0.25	0.12
KNO_3	101.11	0.50	0.25	0.50
K_2SO_4	174.25	0.80	0.20	0.07
$CaCl_2.6H_2O$	219.08	35.00	8.75	3.83
Ground water D				
$NaHCO_3$	84.01	40.29	20.15	3.39
$MgCl_2.6H_2O$	203.31	6.30	1.58	0.64
NaCl	58.44	1.71	0.86	1.01
$CaCl_2.6H_2O$	219.08	27.00	6.75	2.96
$Fe(NO_3)_3.9H_2O$	404.02	5.91	0.99	0.80
Na_2SO_4	142.04	5.00	1.25	0.36
$NaNO_3$	85.00	5.00	2.50	0.43

the lifetime of the waste form. For longer periods however, some considerations must be given to the solution of surface species into the contacting solution and the re-deposition of species from the solution on to the solid surfaces (15).

The experimental conditions are summarised in Table III and the results summarised in Table IV cumulative fractions and Table V diffusion coefficients. As examples, the plots of cumulative fraction leached vs square root of time for polyvinylpyridine resin at both loadings (28% and 40%) in groundwater type C are shown (Fig. 1 and 2). It can be seen that in this case good reproducablity was obtained and equilibrium had been reached after two months.

DISCUSSION

The leaching characteristic of Tulison A27 MP resins containing pertechnate were found to be good with 0.9 to 1.3% of the activity released (for both 30 and 40% loading; FCR 853 matrix). The polyvinyl pyridine resin was found to leach to a greater extent with 3% (30% loading) and 4% (40% loading) of the activity released (FCR 853 matrix). The diffusion

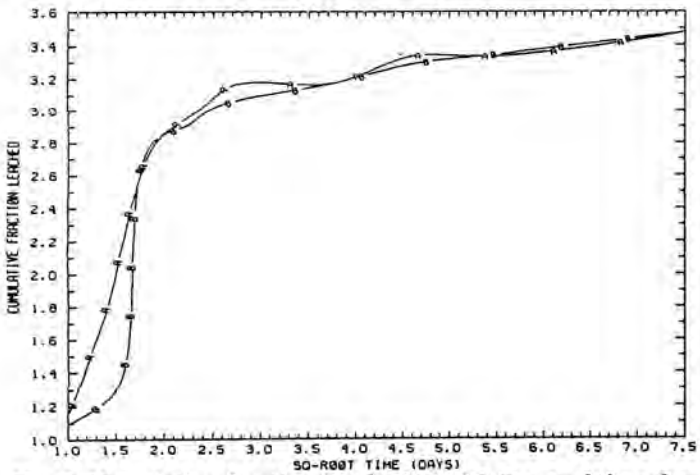

Fig. 1 Cumulative fraction leached Vs SQ-Root of time for polyvinylpyuridine resin in FCR853 matrix, 28% loading, groundwater C.

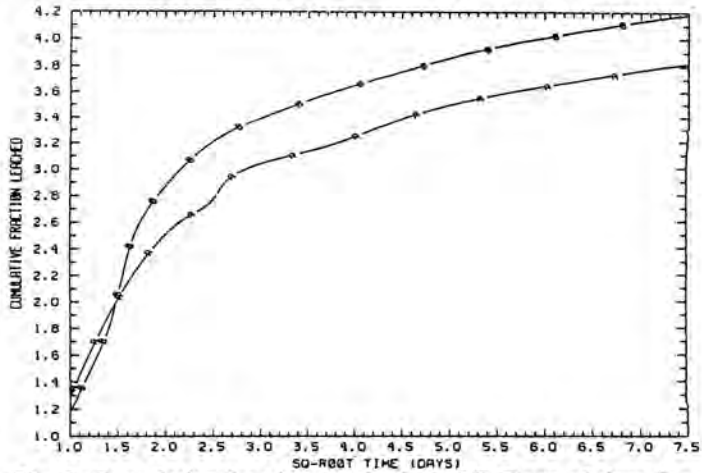

Fig. 2. Cumulative fraction leached Vs SQ-Root of time for polyvinylpyridine resin FCR853, 40% loading, groundwater C.

TABLE III

Experimental Conditions

Dimensions of waste form	12mm x ϕ 30mm
Volume of waste form	8.5×10^{-6} m^3
Temperature of leach test	26 $\pm$ 0.5 °C
Volume of leachant	2.0×10^{-4} m^3
Volume of leachant sampled	5×10^{-7} m^3
Counting solution	Toluene + PPO 60% Triton x 100 30% Water 10%
Volume counting solution	4.5×10^{-6} m^3
Matrix preparation	Cured in water saturated atmosphere at laboratory ambient temperature for 28 days.
Sampling frequency (replacement of leachant)	Daily for seven days Weekly for three weeks Monthly for two months
Leachant container	Polyproplyene
Position of waste form	Suspended from lid of vessel > 500mm below surface of leachant solution

TABLE IV

Percentage of the Initial Inventory of Pertechnate Leached after 54 Days

Sample No.	Cumulative fraction leached	Sample No.	Cumulative leached
Resin 12		Resin 5	
1A	2.4	25B	0.8
2A	1.9	26B	0.9
3A	3.3	27B	0.8
4A	2.9	28B	0.7
5B	4.6	29C	1.0
6B	5.8	30C	1.3
7B	5.0	31C	1.1
8B	5.0	32C	1.0
9C	3.4	33D	1.0
10C	3.4	34D	0.9
11C	4.1	35D	1.3
12C	3.9	36D	1.3
13D	4.8	37E	1.6
14D	4.6	37E	1.1
15D	5.1		
16D	5.0	Resin 12	
17E	4.5		
18E	4.7	39A	2.3
19E	3.6	40A	2.3
20E	3.8	41B	3.7
		42B	5.6
Resin 5		43C	1.5
		44C	5.1
21A	1.1	45D	3.3
22A	1.1	46D	3.5
23A	1.3	47E	1.7
24A	1.2	48E	1.4

Sample Nos. 1 to 20 Polyvinyypyridine groundwater C
21 to 38 Tulison A27MP groundwater C
39 to 48 Polyvinylpyridine groundwater D

A = BFS, B = FCR851, C = FCR853, D = FCR854, E = FCR864

TABLE V

Diffusion Coefficients for Leaching of Pertechnate (TcO^-_4)

Sample No.	Resin No.	Matrix	Loading %	Diffusion Coefficient $m^2\ s^{-1}(x\ 10^{-11})$
1	12	BFS	28	3.18
2	12	BFS	28	3.26
3	12	BFS	40	3.30
4	12	BFS	40	3.14
5	12	FCR851	28	2.53
6	12	FCR851	28	2.35
7	12	FCR851	40	2.36
8	12	FCR851	40	2.32
9	12	FCR853	28	3.13
10	12	FCR853	28	3.14
11	12	FCR853	40	2.65
12	12	FCR853	40	2.64
13	12	FCR854	28	2.59
14	12	FCR854	28	2.77
15	12	FCR854	40	2.36
16	12	FCR854	40	2.36
17	12	FCR864	28	3.10
18	12	FCR864	28	2.97
19	12	FCR864	40	3.14
20	12	FCR864	40	2.03
21	5	BFS	28	2.41
22	5	BFS	28	2.41
23	5	BFS	40	2.34
24	5	BFS	40	2.34
25	5	FCR851	28	1.23
26	5	FCR851	28	0.89
27	5	FCR851	40	2.28
28	5	FCR851	40	2.20
29	5	FCR853	28	2.34
30	5	FCR853	28	2.31
31	5	FCR853	40	2.30
32	5	FCR853	40	2.36
33	5	FCR854	28	2.22
34	5	FCR854	28	2.23
35	5	FCR854	40	2.23
36	5	FCR854	40	1.71
37	5	FCR864	28	2.36
38	5	FCR864	28	2.36
39	12	BFS	28	1.14
40	12	BFS	28	1.26
41	12	FCR851	28	2.40
42	12	FCR851	28	0.13
43	12	FCR853	28	2.36
44	12	FCR853	28	0.80
45	12	FCR854	28	0.41
46	12	FCR854	28	0.55
47	12	FCR864	28	1.27
48	12	FCR864	28	2.22

coefficient of pertechnate from these matrices was found to be in the range 2 to 3E-11 m^2S^{-1}. The leaching of pertechnate from resins in a BFS:OPC matrix was found to be comparable in the case of Tulison A27 MP and superior in the case of the polyvinyl pyridine resin.

CONCLUSION

In conclusion it can be said that for ordinary bead type ion-exchange resins there is some benefit in the use of polymer additives in the cement matrix but further study is required. For resins of the polyvinyl pyridine type no benefit was found in using polymers.

ACKNOWLEDGEMENT

Financial support (D.F.McG) for the duration of this work from HMIP is gratefully acknowledged. The views expressed herein do not necessarily reflect UK Government policy. We thank the resin manufacturers and Liquid Plastics, Preston for the gift of samples.

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