

ACTIVITY REMOVAL FROM LIQUID STREAMS BY SEEDED ULTRAFILTRATION

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ABSTRACT

Modern cross-flow filtration techniques allow the removal of very fine particles of solid material from aqueous streams. When the streams contain radionuclides, some small additional activity removal may be achieved by cross-flow filtration even after the stream has been treated by conventional filtration and ion exchange and despite the concentration of radionuclides being exceedingly small. Much greater activity removal may be achieved if the stream is dosed with additives which absorb or coprecipitate the radionuclides. Individual seeds are, in general, targeted on specific radionuclides (nickel hexacyanoferrate(II) is specific for caesium for instance) and are unlikely, therefore to offer an across-the-board approach to activity removal. Combinations or cocktails of seeds may, however, allow such an approach and this possibility is being investigated.

INTRODUCTION

Ultrafiltration is a relatively new development in filtering science that promises to give much better separations of small particles from aqueous streams than has hitherto been possible. Large scale applications to date have been mainly in the dairy and food industry; the process is, however, largely untested in the nuclear industry, though it forms a key part of the Enhanced Actinide Removal Plant (EARP) being built at the British Nuclear Fuels plc Sellafield site.

The aqueous waste streams arising at nuclear power plants are typically contaminated with very low levels of radioactive nuclides and, when necessary, these are treated by conventional filtration and ion exchange prior to discharge to the environment. Many of these radionuclides are insoluble and so potentially can be readily removed by ultrafiltration. Soluble species cannot be filtered directly, but if additives or "seeds" which absorb the species are added then even soluble radionuclides can be dealt with. Seeds specific to a number of radionuclides have been identified (eg nickel or copper hexacyanoferrate(II) for Cs¹³⁷) and optimum conditions of, for instance, pH and concentration identified [1]. The use of a mixture or cocktail of seeds to remove a variety of radionuclides simultaneously is an obvious extension of the seeded ultrafiltration principle. The seed materials can enhance radionuclide removal by one of three basic mechanisms: precipitation, co-precipitation or absorption. Precipitation and co-precipitation imply the generation of insoluble species in the aqueous waste either by pH change or addition of suitable chemicals in solution. With absorption, however, pre-formed solid material, or more usefully slurries of solid material, can be added to the aqueous waste to be treated. The absorption process is usually one of ion exchange (eg with surface hydroxyls) and this is generally the most versatile and useful

of the three basic mechanisms. Seeded ultrafiltration is thus a novel way of utilizing ion exchange materials.

In an earlier paper [2] we reported our observations on the performance of different seeds used singly or in combination. This paper presents the results of further studies in this field with particular reference to the effect of pH and to the use of zirconium phosphate as an absorber.

EXPERIMENTAL

Apparatus

The ultrafiltration tests were carried out in small rig consisting of a solution reservoir, a pump (Micropump type 120-445-10A) and a 140mm long x 5mm internal diameter (inner surface area 22cm²) vertically mounted ultrafiltration membrane as shown diagrammatically in Fig. 1. The unit was constructed of stainless steel, apart from the inlet and outlet tubes which were polyethylene.

A variety of ultrafilter membrane materials is available. This study has been conducted with a "Carbosep" M4 membrane, consisting of ZrO₂ on a carbon support, with a nominal pore size of 2nm (molecular weight cut off 20,000). The operating pressure was 20psi (1.3 bar), well below that likely to produce a rapid build up of a fouling layer. Dead space in the system was 30ml (~10% of the feed volume) and permeation rates were 100ml h⁻¹ (~1.0m³/m²/d). After each experiment the membrane was washed clean by pumping first 0.5M nitric acid for one hour, followed by 0.5M sodium hydroxide solution for one hour and then by distilled water for one hour. At the start of each new experiment the membrane was conditioned by pumping through water adjusted to the pH of the experiment by the addition of sodium hydroxide or nitric acid. This procedure has been found to

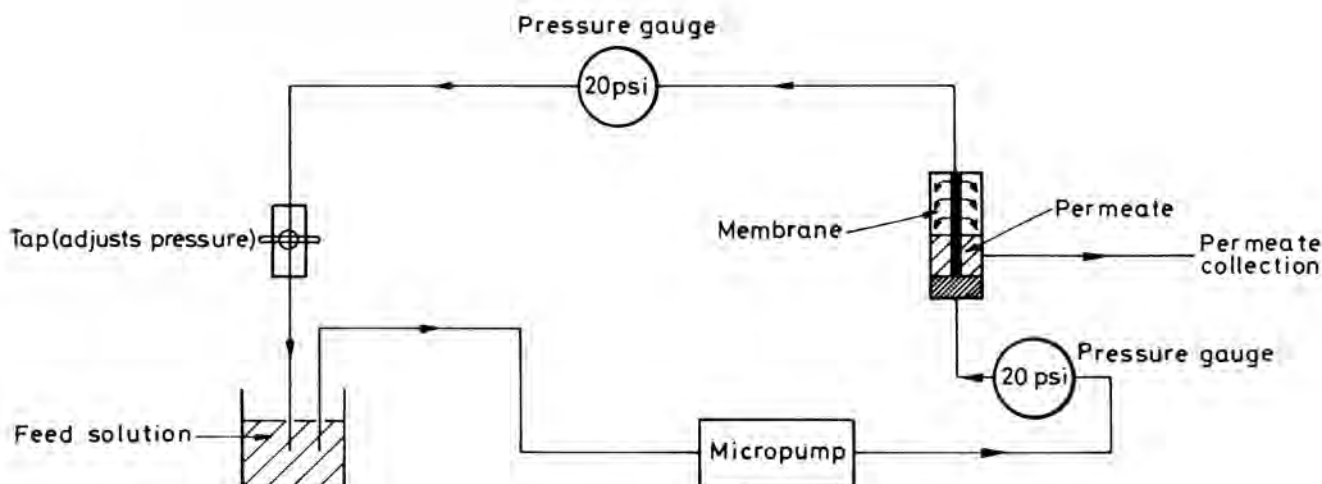


Fig. 1. Schematic diagram of small scale ultrafiltration unit.

clean the membrane very effectively, removing >95% of any adherent material.

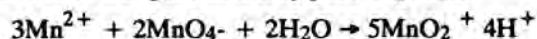
Materials

The four seed materials considered here were prepared as follows:

Sodium Nickel Hexacyanoferrate(II) (NHCF): Equal volumes of 0.094M $\text{Na}_4\text{Fe}(\text{CN})_6$ and 0.113M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions were mixed well and a portion of the resulting slurry was added to the waste simulant to provide the required $\text{Fe}(\text{CN})_6^{4-}$ concentration. The nominal composition of the nickel hexacyanoferrate as prepared was $\text{Na}_{1.6}\text{Ni}_{1.2}\text{Fe}(\text{CN})_6$. (In practice the composition of the precipitated material does not follow exactly that of the solutions as made up - but for the present purposes this is irrelevant.)

Manganese Dioxide (MnO_2): 20ml of an aqueous solution of potassium permanganate (14.4g KMnO_4 per litre) were adjusted to pH11 using sodium hydroxide solution. 400mg of solid sodium dithionite were then slowly added over 15-20 minutes whilst maintaining the pH at 11 ± 0.5 . The slurry was centrifuged and then washed with water adjusted to the pH of the solution to be treated. Addition of the precipitate to 1 litre of solution gave a manganese concentration of 100ppm. Lower concentrations were obtained by slurrying the precipitate of MnO_2 in 20ml of distilled water and taking an appropriate aliquot.

A number of experiments were carried out with a sample of MnO prepared by an alternative route involving the oxidation of manganous ion by permanganate.



1ml of a manganese nitrate solution (93.8g $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ per litre) was added to 10ml of a potassium permanganate solution (3.45g KMnO_4 per litre). The slurry was centrifuged and then washed with water adjusted to the pH of the solution to be treated. Addition of the precipitate to 300ml of solution gave a manganese concentration of 100ppm.

Hydrous Titanium Oxide (HTiO): 10ml of a 15% w/v titanium sulphate solution were treated with 1M sodium hydroxide solution until no further precipitate formed. The precipitate was centrifuged, washed with water to remove excess alkali and then washed with water adjusted to the pH of the solution to be treated. The slurry was then made up to 10ml with distilled water. 1ml of this slurry when added to 300ml of solution gave a titanium concentration of 100ppm.

Zirconium Phosphate (ZrP): 0.1M orthophosphoric acid was added dropwise to a solution of 1.12g of zirconium nitrate [$\text{Zr}(\text{NO}_3)_4$] in 100ml of water. The precipitate of $\text{Zr}(\text{HPO}_4)_2$ was filtered off and washed with water. The washed precipitate was slurried in 100ml of water; 1ml of this slurry when added to 300ml of solution, gave a zirconium concentration of 100ppm.

For the multiple seeding trials the seeds were added in the following order: nickel hexacyanoferrate(II), hydrous titanium oxide, manganese dioxide, zirconium phosphate.

In this work the term "1ppm of absorber" means:

for NHCF	4.7 μ molar
for MnO ₂	18.2 μ molar
for HTiO	20.8 μ molar
for ZrP	11.0 μ molar

Feed solution: All experiments were carried out with a simulated waste having the composition shown in Table I. The isotopes were as supplied by Amersham International and were present as either their chloride or nitrate salts.

TABLE I

Composition of Waste Simulant Solution (pH7)

Nuclide	Activity (Bq l ⁻¹)	Nuclide	Activity (Bq l ⁻¹)
Cr ⁵¹	41100	Nb ⁹⁵	8000
Mn ⁵⁴	25200	Ru ¹⁰⁶	3200
Fe ⁵⁹	6700	Agm ^{110m}	22500
Co ⁶⁰	24200	Sb ¹²⁵	98400
Zn ⁶⁵	6100	Cs ¹³⁷	84000
Sr ⁹⁰	80	Ce ¹³⁹	3900

Procedure

Concentrations of gamma-emitting nuclides were determined by high resolution gamma spectrometry using an EG and G Ortec Gamma X HP Ge coaxial detector coupled via a Model 918 Adcam multichannel buffer to a Digital PC 350 computer. Strontium analysis was achieved by counting SrCO₃(s) samples after radiochemical separation from the test solutions using a carrier. The samples were then counted in a Sugarman detector under a methane/argon atmosphere.

Radionuclide concentrations were determined in the feed and permeate for all runs and these values used to determine the decontamination factor (DF) defined as follows:

$$DF = \frac{\text{feed activity (Bq ml}^{-1}\text{)}}{\text{permeate activity (Bq ml}^{-1}\text{)}}$$

RESULTS

The results obtained in earlier studies on seeded ultrafiltration [2] were all obtained at a solution pH of 7 and indicated that sodium nickel hexacyanoferrate(II) used in combination with either hydrous titanium oxide or manganese dioxide might give the best overall reduction in activity. We have now examined the effect of solution pH on the

performance of these three absorbers when used in combination. Table II lists the DF obtained for each of the thirteen radionuclides present in the test solution; it is apparent that solution pH has a marked effect on the decontamination achieved. For comparison purposes, the DFs obtained by ultrafiltration alone at solution pHs of 3, 7, 9 and 10.5 were determined and the values obtained are presented in Table III.

TABLE II

Decontamination Achieved by Seeded Ultrafiltration - Effect of pH

Seeds	ppm	ppm	ppm
NHCF	10	10	10
MnO ₂	20	20	20*
HTiO	20	20	20
Nuclide	Decontamination Factor		
Cr-51	2.0	1.1	798
Mn-54	6.7	211	978
Fe-59	3.2	2.1	> 12
Co-60	21	49	153
Zn-65	56	15	> 5
Sr-90	2.3	4.0	-
Zr-95	2.1	2.0	57
Ru-106	3.9	1.4	6.3
Ag-110m	98	8.3	5.1
Sb-125	1.1	1.1	2.3
Cs-137	69	216	1.0
Ce-139	3.1	12.3	> 4
pH	7	9	10.5

NHCF = sodium nickel hexacyanoferrate(II)

MnO₂ = manganese dioxide

HTiO = hydrous titanium oxide

* = MnO₂ from Mn²⁺ + MnO₄⁻

TABLE III

Decontamination Achieved by Ultrafiltration -
Effect of pH

Nuclide	Decontamination Factor			
	3	7	9	10.5
Cr-51	1.4	1.3	1.1	15.7
Mn-54	1.0	3.8	3.8	241
Fe-59	>5	5.6	1.6	1.6
Co-60	1.0	4.1	2.8	149
Zn-65	1.0	16	3.6	>6
Sr-90	-	2.3	2.7	1.8
Zr-95	>14	1.5	1.6	13.7
Nb-95	>22	1.3	-	-
Ru-106	2.4	1.6	1.4	4.0
Ag-110m	4.4	>21	48	7.0
Sb-125	4.2	1.0	1.0	2.5
Cs-137	1.1	1.1	1.0	1.0
Ce-139	>5	27	8.2	1.1
pH	3	7	9	10.5

Assuming that a DF of 10 (90% removal) for each radionuclide is the minimum requirement for the decontamination treatment, it is possible to compare and contrast simple ultrafiltration with seeded ultrafiltration using the three-component seed cocktail. Table IV shows this comparison and it is apparent that seeded ultrafiltration is more effective than ultrafiltration alone and that more nuclides are reduced to low levels by increasing the pH of the solution. However, the range of nuclides removed also varied with solution pH, in particular, caesium is effectively removed at pH7 and 9 by the seeds but not at 10.5. This change in behavior is due to decomposition of the NHCF at pH10.5 to produce sodium ferrocyanide and nickel hydroxide.

TABLE IV

Comparison of Ultrafiltration and Seeded Ultrafiltration
- Effect of pH

Nuclide	Ultrafiltration only			with seed cocktail			
	pH	7	9	10.5	7	9	10.5
Cr-51				✓			✓
Mn-54				✓		✓	✓
Fe-59							✓
Co-60				✓	✓	✓	✓
Zn-65	✓	✓			✓	✓	(✓)
Sr-90							
Zr-95				✓			✓
Nb-95							
Ru-106							
Ag-110m	✓	✓			✓		
Sb-125							
Cs-137					✓	✓	
Ce-139	✓	✓				✓	(✓)

✓ = DF ≥ 10

(✓) = reduced to below limit of detection

seed cocktail = 10ppm NHCF, 20ppm HTiO, 20ppm MnO₂

Zirconium Phosphate

Zirconium phosphate (ZrP) is probably the most thoroughly studied inorganic ion-exchanger and a large number of articles have been published [3]. Table V shows the results obtained in a small program of experiments to examine the performance of ZrP on its own and in combination with NHCF or HTiO; the decontamination achieved by ultrafiltration alone is included for comparison. From these results it is apparent that ZrP has a strong affinity for manganese, cobalt, zinc, silver and cerium and a moderate affinity for strontium and zirconium. When used in combination with NHCF, a high DF for caesium is also obtained. The combination of HTiO and ZrP shows little improvement over ZrP alone.

DISCUSSION

All the absorber materials tested in this study have enhanced the removal of some of the thirteen radionuclides present in the test solution. The radionuclides which have proved the most difficult to remove in our tests are Cr⁵¹, Sb¹²⁵ and to a lesser extent Ru¹⁰⁶; these are present in our solutions in anionic form (as they would be in real effluents). Absorbers for anionic species need therefore to be identified or the possibility of converting these species to cationic form, for instance by reduction, needs to be considered. Operation at pH10.5 appears to give good removal of chro-

TABLE V

Results from Recent Experiments at pH7

Seed	ppm	ppm	ppm	ppm	UF only
NHCF	-	-	10	-	
HTiO	-	-	-	100	
ZrP	10	100	100	100	
Nuclide	Decontamination Factor				
Cr-51	3.3	4.9	2.4	3.3	1.3
Mn-54	56	297	633	154	3.8
Fe-59	3.8	6.1	7.3	4.5	5.6
Co-60	85	323	584	140	4.1
Zn-65	>100	>100	>100	191	16
Sr-90	7.5	18	22	42	-
Zr-95	6.6	11	25	31	1.5
Ru-106	2.2	3.4	2.3	4.2	1.6
Ag-110m	>21	>21	>21	>21	>21
Sb-125	1.0	1.2	1.1	1.5	1.0
Cs-137	1.2	2.2	149	1.6	1.1
Ce-139	22	45	49	27	27

NHCF = sodium nickel hexacyanoferrate(II)

HTiO = hydrous titanium oxide

ZrP = zirconium phosphate

mium but decomposes the NHCF; so far, NHCF is the only absorber we have found to have a strong affinity for cesium.

From a radiological standpoint (that is in terms of dose to critical groups) the most important radionuclides likely to occur in nuclear power station liquid effluents are Cs¹³⁷ and Co⁶⁰. No single seed can reduce both these, but a mixture of, for instance, NHCF and HTiO or ZrP can provide reductions of at least 98% (DF > 50). Incorporation of MnO₂, prepared from Mn²⁺ and MnO₄⁻, provided reductions in a broader spectrum of radionuclides, but several important ones are only reduced by a small amount and only low overall DFs for $\beta\gamma$ activity can be achieved with the simulant we have investigated. Further novel absorbers need to be identified especially if large reductions (eg DF > 10) in total activity are to be achieved.

This study has been concerned specifically with the reduction of already very low concentrations of radionuclides from nuclear power station effluents but there is no reason why aqueous wastes contaminated with even quite low levels of other materials, such as transition metal ions, should not be treated in a similar manner. The correct choice of seeds is essential if a variety of different species are to be treated simultaneously. In effect, seeded ultrafiltration offers a way of tailoring ion exchange to the treatment of complex mixtures of chemicals. Although not considered here, it is generally possible to achieve higher

absorption efficiencies (amount of material absorbed per unit of absorber) with UF seeds than in conventional ion exchange beds. Seeded UF also does away with the need for the material to be granular in form and of sufficient strength that it could be used in a conventional ion exchange bed (often a problem with inorganic absorbers), and in principle allows a wider range of absorbers to be considered.

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