Lecture Theatre A 8pm

HP4351 1030

SNO-STR-95-019

No figures

Conductivity, R/O, [illegible]

hollow fibre degassing

[illegible]

heating

Schedule meeting

An investigation of SUF at the 100l scale

R.Taplin*

March 17, 1995

Fines To be done. HTiO2 on membrane 1 none on membrane 2

See how much activity on membrane 2.

pH4 Ra not removed.
pH7 Ra is removed.

Introduction

Ts decay tech necessary

Seeded ultra-filtration (SUF) using hollow fiber membranes loaded with hydrous titanium oxide (HTiO) seems to offer the SNO collaboration a quantitative method for the simultaneous extraction and assay of members of the ^{232}Th and ^{238}U chains present in samples of heavy water. The assay of radium and lead is also possible, and thus so is the study of any disequilibria within the chains. The extraction can be followed by the counting technique devised by the author: delayed β-α coincidence in a liquid scintillator. So far no major problems (eg backgrounds, fines, efficiency) have been encountered, although experiments continue at Oxford in order to confirm the method at the levels required for the detector.

In order to assess the performance of SUF for the detector water system, lab-scale experiments are needed. Although such experiments are a very long way away from the conditions arising in the detector system, such calibration is necessary in order to test various hypotheses. The exact factor by which the experiments is scaled is not obvious, but for the purposes of SUF the measuring unit is the amount of water passing unit area of membrane per unit time. This has the dimensions of a flow velocity per metre squared, and for the system proposed for the detector this works out as 40 litres per minute per metre squared of H_2O at 20 degrees centigrade.

Thus, for a 300 cm^2 surface area membrane[1], this required flow rate is 1.2 l/min. The largest convenient volume currently available[2] in Oxford is around 100l, which

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*Much of the early work was completed under the aegis of M.E.Moorhead, to which a grateful acknowledgement should be extended.

[1] Such a membrane is referred to as a 1ft membrane due to the length of the cartridge, whereas the 2.5 m^2 membranes in the detector system are known as 4ft membranes.

[2] As at Winter 94. Work has now (3/95) begun on the 2xH1 in series system detailed towards the end of the report.

corresponds to around 20 tonnes of D_2O after the scaling is applied. This 100l plant was used in some preliminary tests of a new membrane.

The single H1 tests

In order to check decontamination factors (DF's) of up to 100, the 100 litres process volume was spiked with around 1 kBq of ^{228}Th. This allowed samples of the feed and permeate to be taken from the apparatus and subsequent counting of up to 12 ml of these streams using the two inch PMT liquid scintillator system currently running at Oxford. Such a spike is equivalent in the feed stream to around 1000 decays per day per milliliter, which is still a very long way from the 1 decay per day per tonne needed in the detector.

The plumbing for the system is shown in figure . The system is slightly over-complicated in order that many different operations could be done without having to break any tubing in the system. The detailed explanation of the function of all the valves is somewhat tedious, and is not included here.

Tests concentrated mainly on the performance of a new membrane, the Amicon H1MP01-43. This membrane has 0.03 m^2 surface area, while the pores are 0.1 micron in diameter. The large pore size compared to the previously used 30 kilo-Dalton (around 5 nm) membranes means that, for the same trans-membrane pressure, much more water can be passed with the same membrane area. In the detector water system this cuts down the number of cartridges needed from 4 to 2, and hence leads to a reduction by a factor of two such problems as membrane cleanliness and hold-up volumes.

Previous work had suggested that an amount of HTiO equivalent to 0.5 grammes per m^2 membrane area led to high extractions even in water with a fairly high ion content. For these experiments the current RO system at Oxford was polished with a mixed resin ion exchanger to around 10 MΩ, which although fair, is still a long way in terms of ion content from the purest water. Ion content affects SUF adversely in that metals such as iron and calcium are taken up by the HTiO, so leading to a drop in the extraction of the radionuclides.

The HTiO was deposited on the membrane by recirculating a colloidal solution through the membrane. The particulate HTiO deposits onto the inner surface of the hollow fibres and samples of the solution were taken for spectroscopic titanium analysis in order to quantify the amount of titanium on the membrane.

The spike was taken from the source bottle and counted using a GeLi gamma counter. The spike was added to the 100 litre volume which was then neutralised to pH 7 using sodium hydroxide. The addition of sodium ions is not important as the

HTiO does not extract the lightest group I elements. Pumping then began at 1.2 l/min, with the trans-membrane pressure adjusted so as to give this flow rate. The membranes were used in 'dead-end' mode, whereby there is no recirculation on the retentate side, and all the water delivered to the membrane is pushed through to the permeate side. This did lead to some problems due to air bubbles in the feed stream. These would collect within the fibres themselves, and hence reduce the active area of the membrane. Consequently, at predetermined intervals the pump speed was turned down and the back pressure tap was opened so as to flush the air out of the fibres. The back pressure tap was then closed, and the pump brought back up to speed. The detrimental effects of this process were checked by collecting the water flushed away by this process, and analyzing for both titanium and radioactivity.

During the run samples were taken both from the permeate line and the feed tank. The feed tank was stirred briefly before taking the sample in order to make sure that the radionuclides were well mixed. Samples were taken after 10, 50 and 90 litres of the process volume had passed through the membrane. With a flow rate of 1.2 l/min, the processing of the volume took around 1.5 hours. The pump was then stopped and the first elution took place.

Previous work with HTiO had shown that nitric acid of around 0.03M concentration eluted practically all the radium (both 224 and 226) in 15 minutes with only around 5% of the titanium being dissolved. However, the corresponding efficiencies for ^{212}Pb and ^{228}Th with this acid are only around 10%, and so another acid is needed for the removal of ^{228}Th and ^{212}Pb. Subsequent work by the author led to the use of 0.5M hydrochloric acid to remove both ^{228}Th and ^{212}Pb. This strength of acid is such that much more titanium is dissolved, and so a much shorter time of elution is necessary to get the greatest radionuclide to titanium ratio in the acid. An elution time of 5 minutes was decided upon, during which around 75% of the ^{228}Th and ^{212}Pb are removed, with around 25% titanium. This also removes around 70% of the ^{224}Ra. The extraction of ^{224}Ra to a higher level may be possible by carrying out two separate elutions: first the 0.03M HNO_3 wash for around 15 minutes which will remove the radium, followed by the 0.5M HCl wash which will remove the thorium and lead.

In these experiments, the first elution thus consisted of 300ml of 0.5M HNO_3 run for 5 minutes. This high volume was dictated by the large amount of pipework associated with the rig. After pumping stopped, the acid was drained out of the system, and 50ml of the acid were used for gamma counting, a process which is detailed below.

The second elution consisted of 400ml of 0.5M HCl run for around one hour. This was to remove the remaining titanium and also to check elution efficiencies, as any remaining activity should come off with this wash. A third elution was also deemed necessary after the first experiment, as the low solubility of the titanium is such that it can precipitate out even in 0.5M HCl. Again, this wash lasted around 1 hour. After flushing the membrane system with water to bring the pH in the reservoir to around 6, the feed tank was rinsed with 0.5M HCl. This was done by putting around one litre of acid into the tank and spraying the sides through a nozzle. This was to ensure a high removal of any plated radionuclides into as small a volume as possible. After around 10 minutes of spraying, the acid was removed and the feed tank was rinsed with water to around pH 6.

The final process carried out on the membrane was recirculation cleaning. This employs a very fast pumping speed which establishes a pressure drop along the length of the fibres in the membrane. If the permeate side of the cartridge is filled with liquid then closed to the atmosphere a pressure differential drives liquid out of the pores at the high pressure end of the fibre and pushes the same liquid back into the fibre at the low pressure end. This process is usually carried out with 0.1M sodium hydroxide, a recommended cleaning fluid, and is intended to restore the permeate rate. In order to clean the membrane properly, the flow along the inside of the fibre has also to be reversed, so that the fluid is pushed into both ends of the fibre. After a suitable cleaning period, the hydroxide is drained and a sample reserved for counting, while the rest of the system is flushed back to pH 7 with repeated treatments of water.

The samples thus generated by a single run allowed the determination of possible chemical effects which could lead to misleading results, the most obvious of these being plating of radionuclides. The feed and permeate samples were used to make scintillation sources and these were counted almost immediately after production in order to avoid the loss of the faster ^{212}Pb decays. The samples were generally counted for around 4 days. After a few weeks, the sources were counted again for a few days. This allows the determination of ^{212}Pb, ^{224}Ra and ^{228}Th levels in the samples after log-likelihood fitting of the time spectrum of counts. The gap in the counting does not really affect the accuracy of the fitting, as enough information is contained in the first 3 to 4 days to allow a good determination for ^{224}Ra.

The other samples were counted on the gamma counter using the 583 KeV line from ^{208}Tl. In order to measure the approximate amounts of ^{212}Pb, ^{224}Ra and ^{228}Th the samples were counted at 3 hours, 3 days and 2 weeks after production respectively. The ^{212}Pb counting was left for a few hours as the 583 KeV line from ^{208}Tl line was used, and the intermediate bismuth was thus allowed to equilibrate in this time. If the amounts of ^{212}Pb, ^{224}Ra and ^{228}Th do not differ too much from equilibrium then after 3 days the thallium is in approximate equilibrium with the ^{224}Ra, and similarly

=[taplin.sno,*tuff.psfiles*]*pipework.eps*

Figure 1: The plumbing for the single H1 tests.

for the ^{228}Th after two weeks.

The final measurements made for each experiment were the spectroscopic analyses of the titanium concentration. By the addition of a sample containing titanium to a mixture of sulphuric acid and hydrogen peroxide a yellow species is formed, the strength of the colour being directly proportional to the amount of titanium. The colour is quantified by measuring the absorbtion at 410nm using a spectrophotometer and calibrated against standard samples of known titanium concentration. This allowed the measurement of the amounts of titanium in various samples down to the few ppm level.

Results

The first experiment, NS1[3], did not actually use the new MP01 membrane but an older P30 membrane instead. This 30 kDalton membrane was used to check the system could perform as expected and allowed a comparison with previous results. Owing to a slight miscalculation of the feed activity, only around 50 Bq of ^{228}Th were used. The counting of the feed and permeate were consequently slightly more uncertain than usual, but reasonable DF's were obtained. The gamma counting and titanium analysis results are shown in tables 1 and 2. The figures for the DF measurement are in table 3.

The final column in table 1, Tl adjusted, refers to the total amount of activity in the whole of the sample. Since the minimum elution volume of the system was 300 ml,

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[3] The prefix NS refers to New membrane Seeded ultrafiltration

Sample Name	Description	Time of Counting	Tl c/ks	Tl adjusted c/ks
Feed 0	Feed source	12:45 - 10/8	448±16	450±20
EL 1	First elution	18:44 - 10/8	56.3±5.7	340±30
EL 1	First elution	18:59 - 12/8	61.1±6.2	370±40
EL 1	First elution	12:24 - 24/8	32.9±6.0	200±40
EL 2	Second elution	14:43 - 24/8	20.7±4.7	170±40
FTR	Rinse of tank	19:17 - 10/8	5.4±3.5	48±31
FTR	Rinse of tank	19:17 - 12/8	7.7±3.5	68±31
FTR	Rinse of tank	14:05 - 24/8	2.5±2.0	22±18

Table 1: Experiment NS1 - H1P30-20 membrane - Gamma counting.

Sample name	Titanium measured /ppm	Titanium adjusted /ppm	Titanium total /mg
Before deposit	18.9	47.3	23.7
After deposit	0.4	1	0.5
EL 1	6.0	15	4.5
EL 2	11.5	29	11.5

Table 2: Experiment NS1 - H1P30-20 membrane - Titanium analysis.

and the gamma counting is standardized on 50 ml vials, only one sixth of the sample could be counted. Hence the last column in this table shows a multiplication of six for the EL1 entries. All subsequent tables will have these two columns, although the multiplications will not be mentioned explicitly. The former of the two columns is included so as to allow the comparison of the measured numbers with the background of the GeLi, which was measured at around 5 c/ks.

The titanium analysis table shows the amount of titanium measured in a test volume, the parts per million in the sample under test and the total mass of titanium in the total volume. The before and after deposit samples were small (10 ml) samples of the reservoir (500 ml) taken before and after the HTiO deposition respectively. Again, the titanium measured column is included as these measurements have an uncertainty of around 1ppm.

The DF measurement table shows only the final determinations for the DF's. The figure of >100 is given for all permeate samples where the extraction was better than 99%, in order to remove any poor fitting which occurs when the amount of radium is so small.

As can be seen, the elution efficiency for ^{212}Pb and ^{224}Ra is around 75%, whereas for the ^{228}Th the first elution only removes around 50%. This does not correspond too well with the batch contact experiments done previously, although the difference between batch contact and membrane work had been seen in many cases previously. The second elution does remove most of the remaining ^{228}Th however, and so the membrane can be said to be clean of the majority of the activity deposited onto it. The amount of plating of all three radionuclides is not large, although the numbers above are very close to the background of the GeLi.

The overall impression from this experiment is that the membrane behaves fairly well. The DF's are high and, at least for ^{224}Ra and ^{228}Th, seem to remain so during the run. The elution of the radionuclides removes a large fraction of the activity with a small amount of titanium, and for the detector system makes second stage concentration that much easier. However, there are two outstanding problems: the first is that the ^{212}Pb DF drops to around 10, and the second is the low amount of titanium recovered in the acid washes. This first problem was seen in all subsequent experiments, and is dealt with in a separate section under the heading of radon breakthrough. The missing titanium is more of a problem, as if titanium is left on the membrane it will eventually block the pores and lead to a drop in membrane throughput. At this point the loss of titanium was put down to the acid wash not being strong enough, and a third acid wash was instituted for the subsequent experiments.

Sample Name	Litres passed when taken	^{228}Th DF	^{224}Ra DF	^{212}Pb DF
Perm 1	10	85	>100	48
Perm 2	50	81	>100	18
Perm 3	90	60	>100	13

Table 3: Experiment NS1 - H1P30-20 membrane - DF measurements.

Sample Name	Description	Time of Counting	Tl c/ks	Tl adjusted c/s
Feed 0	Feed source	11:45 - 12/8	14600±80	14.6±0.1
EL 1	First elution	17:05 - 12/8	1350±40	10.8±0.3
EL 1	First elution	19:49 - 16/8	857±51	6.9±0.4
EL 1	First elution	09:19 - 30/8	446±19	3.6±0.2
EL 2	Second elution	17:27 - 12/8	164±15	1.3±0.1
EL 2	Second elution	19:59 - 16/8	250±23	2.0±0.2
EL 2	Second elution	09:40 - 30/8	263±16	2.1±0.1
FTR	Rinse of tank	17:34 - 12/8	1062±60	8.5±0.5
FTR	Rinse of tank	19:40 - 16/8	678±43	5.4±0.3
FTR	Rinse of tank	09:52 - 30/8	307±23	2.5±0.2

Table 4: Experiment NS2 - H1MP01-43 membrane - Gamma counting.

The second experiment, NS2, was the first with the new H1MP01-43 membrane. The pores are around 400 times the area of those in the H1P30-20 membrane, and so the desired flow rate of 1.2 l/min could be achieved at a much lower trans-membrane pressure. This was seen, with the P30 needing around 3 bar, while the MP01 needed only around 5 psi to pass 1.2 l/min. This performance improvement is vital, as it reduces the number of cartridges needed for the passage of 200 l/min in the full scale plant.

The same process of deposition and pumping was done with the new membrane, and the results are shown in tables 4, 5 and 6.

The were a number of problems with this experiment. An improper neutralisation of the feed tank led to a large amount of plating in the tank, and this was further accentuated by an excess of ^{212}Pb, which may have been caused by contamination of the feed tank surface. The loss of around half of the titanium was also very worrying as in this case three acid washes were done, and the third showed almost no titanium. This could be attributed to the HTiO breaking-up and going through the membrane, or the formation of insoluble TiO_2. The poor neutralisation of the feed

Sample name	Titanium measured /ppm	Titanium adjusted /ppm	Titanium total /mg
Before deposit	9.2	23	11.5
After deposit	0.18	0.5	0.2
EL 1	1.2	3	1.2
EL 2	5.7	14	5.7
EL 3	0.7	2	0.7

Table 5: Experiment NS2 - H1MP01-43 membrane - Titanium analysis.

Sample Name	Litres passed when taken	^{228}Th DF	^{224}Ra DF	^{212}Pb DF
Perm 1	10	12	>100	36
Perm 2	50	15	>100	25
Perm 3	90	20	37	12

Table 6: Experiment NS2 - H1MP01-43 membrane - DF measurements.

could also have led to the formation of unabsorbable ^{228}Th complexes, leading to the relatively low ^{228}Th DFs. The elution efficiencies were affected by the plating in that it was difficult to estimate how much activity the membrane had seen. The ^{228}Th accountancy was very poor, with around 40% being lost, and, finally, the permeate rate of the membrane dropped by a factor of 3. This meant that to get 1.2 l/min through the membrane now needed around 1 bar trans-membrane pressure.

The third experiment, NS3, was again with the MP01. The feed tank was thoroughly cleaned and checked between NS2 and NS3, as were the titanium measurements. One problem that could not be solved was the drop in membrane throughput. Although it was known that membrane performance decreases with use, this drop was larger than had been seen in previous work.

The results for NS3 are shown in tables 7, 8 and 9.

In this experiment, the elution efficiencies are around 75% for ^{212}Pb and ^{224}Ra, while the accountancy for these two is also close to 100%, given that around 5% of the ^{224}Ra ended up in the permeate stream. The titanium recovered seems much closer to 100%, and the ^{228}Th DFs were about 50. The only two problems are the ^{228}Th accountancy and the fact that the membrane throughput dropped by around another 30%.

The former problem was found to be due to a new ^{228}Th source that had been used for NS2 and NS3. The feed scintillation sources showed that the ^{228}Th activity was around 60% of the activity of ^{212}Pb and ^{224}Ra. This could have been attributed to

Sample Name	Description	Time of Counting	Tl c/ks	Tl adjusted c/s
Feed 0	Feed source	12:30 - 16/8	14500±100	14.5±0.1
EL 1	First elution	18:04 - 16/8	1710±50	10.3±0.3
EL 1	First elution	15:35 - 19/8	1410±50	8.5±0.3
EL 1	First elution	12:34 - 30/8	780±30	4.7±0.2
EL 2	Second elution	18:21 - 16/8	290±20	1.7±0.1
EL 2	Second elution	15:48 - 19/8	360±30	2.2±0.2
EL 2	Second elution	12:57 - 30/8	446±20	2.7±0.1
FTR	Rinse of tank	20:42 - 16/8	40±10	0.7±0.1
FTR	Rinse of tank	14:49 - 19/8	10±5	0.2±0.1
FTR	Rinse of tank	14:45 - 30/8	10±5	0.2±0.1

Table 7: Experiment NS3 - H1MP01-43 membrane - Gamma counting.

Sample name	Titanium measured /ppm	Titanium adjusted /ppm	Titanium total /mg
Before deposit	8.9	22	11.2
After deposit	0.4	1	0.5
EL 1	2.0	5	3
EL 2	6.6	17	10
EL 3	1.1	3	1.7

Table 8: Experiment NS3 - H1MP01-43 membrane - Titanium analysis.

Sample Name	Litres passed when taken	^{228}Th DF	^{224}Ra DF	^{212}Pb DF
Perm 1	10	36	>100	41
Perm 2	50	59	84	22
Perm 3	90	48	7	13

Table 9: Experiment NS3 - H1MP01-43 membrane - DF measurements.

Sample Name	Description	Time of Counting	Tl c/ks	Tl adjusted c/s
Feed 0	Feed source	15:11 - 15/9	1010±50	10.1±0.5
Feed 0	Feed source	14:22 - 19/9	645±35	6.5±0.4
Feed 0	Feed source	10:46 - 30/9	546±30	5.5±0.3
EL 1	First elution	15:16 - 15/9	966±59	7.7±0.5
EL 1	First elution	14:10 - 19/9	610±38	4.9±0.3
EL 1	First elution	10:58 - 30/9	269±24	2.2±0.2
EL 2	Second elution	16:52 - 15/9	147±20	1.2±0.1
EL 2	Second elution	15:14 - 19/9	139±30	1.1±0.1
EL 2	Second elution	11:30 - 30/9	153±20	1.2±0.1
FTR	Rinse of tank	10:15 - 15/9	32±12	0.6±0.2
FTR	Rinse of tank	16:40 - 19/9	19±9	0.4±0.2
FTR	Rinse of tank	16:40 - 30/9	13±7	0.3±0.1

Table 10: Experiment NS5 - H1MP01-43 membrane - Gamma counting.

plating in the 100l feed tank, but the same activity levels were seen in the feed sources taken at 10l and at 90l. This implied that the feed stock that was being added to the 100l tank was deficient in ^{228}Th, and a confirmation of this was found by testing the source bottle. In the subsequent experiment, NS5, around 10% of the feed stock added to the 100l tank was kept and used as a control of the source activity, and this behaviour was observed. The reason for this deficiency in ^{228}Th is not known, but if samples of the feed stock are kept, any disequilibria in the chain can of course be calibrated out.

The final 100l experiment, NS5[4], was carried out with the new arrangement of measuring the feed activity and with the other tighter controls of NS3. The results are shown in tables 10, 11 and 12.

This final experiment was very instructive. The ^{212}Pb and ^{224}Ra elution efficiencies

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[4] NS4 was aborted after the pump broke down half way through the experiment.

Sample name	Titanium measured /ppm	Titanium adjusted /ppm	Titanium total /mg
Before deposit	11.6	29	11.6
After deposit	0.4	1	0.4
EL 1	0.9	2.3	0.9
EL 2	4.3	10.8	4.3
EL 3	0.7	1.8	0.7

Table 11: Experiment NS5 - H1MP01-43 membrane - Titanium analysis.

are both around 75%, while the ^{228}Th is around 50%. The DFs are particularly good, with only the third ^{224}Ra DF falling significantly below 100 (again, the ^{212}Pb DFs will be treated later). The problems of titanium loss, and also membrane throughput appeared again.

This experiment was monitored for membrane throughput for every step of the extraction, to see exactly where the drop occurred. It was observed that the trans membrane pressure needed for 1.2 l/min did not change throughout the pumping of the 100l. This was unexpected, as it is supposed to be the integrated amount of fluid passing the membrane which dictates its throughput. The real drop in membrane performance occurred during the acid washes. After consultation with the manufacturer, Amicon, it was decided that the acid was not attacking the material of the membrane itself. Thus, a new idea was needed.

After much thought, a scheme which linked the acid washes to the loss of titanium was put forward. As the acid dissolves the particulate HTiO, the size of the particles decreases in proportion with the surface area exposed to the acid. The size of the particulate HTiO had been previously measured with a mean of around 10 microns, with tails to 1 and 100 microns. As these particles are dissolved, they reduce in size, and at some point become small enough to lodge in the 0.1 micron pores of the membrane. At this point they see less acid, so their rate of dissolution is greatly reduced. It should be mentioned that during elution, the acid was recirculated with enough back pressure to equalize the flows in the permeate and retentate sides of the circuit. This means that water was being driven through the pores and hence could push the 0.1 micron HTiO particles into the pores.

This was viewed as a good proposition, as it seems to solve the two problems at once. The missing titanium is lodged in pores and only very slowly dissolved by repeated acid washes, and the membrane performance should drop during the elution stages. The recirculation cleaning with sodium hydroxide should remove some of this lodged titanium by pressure, but as the HTiO is stable in alkali, it would not be reduced in size. This was indeed the case, with the recirculation cleaning appearing not to affect the membrane performance. As a final test of the hypothesis, the membrane could be soaked in acid for a long time, and the gradual attack of the lodged particles would be such that the membrane should recover.

The MP01 was thus immersed in 1M HCl, and left to stew for around 1 month. It has recently been tested, and the permeate rate recovered to somewhere near one half of the initial performance when the membrane first had water pumped through it. Such a drop in performance is as expected both from information supplied by the manufacturers, and also with previous experience of other membranes at Oxford.

However, there is just one objection to this scheme. The average size of the particles of HTiO is around 10 microns. If they are reduced to 0.1 microns, the volume reduction is around 1 part in 10^6. This would mean that even if all the HTiO particles were reduced to this size, then we would obtain practically 100% of the Ti. Of course, there is no obvious reason for thinking there is a link between this loss of titanium, and the drop in permeate rate. For example, we could be losing around half the titanium in fines which pass through the membrane, and the subsequent elution blocks the membrane with a tiny fraction of the titanium as detailed above. Work is continuing on a satisfactory explanation of this effect, although there has not been a great amount of progress.

Summary of NS experiments

Overall, these experiments were not particularly successful in themselves, but did allow an investigation of some of the problems of the 0.1 micron membrane hollow fiber cartridges. The problem of HTiO elution and the blocking of the membrane might need much investigation. One proposal is the use of gas pressure on the permeate side so as to stop the small HTiO particles being pushed into the pores, if this is indeed the case. Also, the elution of ^{212}Pb and ^{228}Th, although successful, is still not brilliant, with much more titanium being dissolved off for sensible amounts of radionuclide extraction. On the four foot membranes, this means that the second stage concentration of the ^{212}Pb and ^{228}Th is much more difficult, and may involve two separate steps. This increases the time of concentration, a vital factor in the determination of 10 hour ^{212}Pb. Of course, more stages also inevitably lead to higher backgrounds and increased complexity of operation.

The DFs are all fairly good, although the fall off with time is worrying. This has previously been attributed to ion content in the water being used for the extraction. The drop in ^{224}Ra DF, without a commensurate drop in ^{228}Th DF would seem to lead to this conclusion, as the valence II ^{224}Ra is much more easily replaced by transition metals than the valence IV ^{228}Th. The variation in the final ^{224}Ra DF also probably implies that the water quality varied from run to run. The ^{212}Pb DFs show similar behaviour for all three runs, with the 10 litre samples having DFs of around 50, and the 90 litre samples all coming in at around 10 to 12. This behaviour seemed remarkably reproducible, and as such was worthy of further investigation. This work is shown below.

Radon breakthrough

We begin this section with a theoretical determination of the DF fractions for a 100l run. If we consider the number of atoms, N^F, passing a point just before the membrane, where the superscript F denotes the feed line, the flow rate is:

$$\frac{dN_i^F}{dt} = \left.\frac{\partial N_i^F}{\partial V}\right|_t \frac{dV}{dt} + \left.\frac{\partial N_i^F}{\partial t}\right|_V$$

where i=Th, Ra, Pb. The second term in this equation is set to zero as we only consider small elements of the feed during the run. Thus,

$$\frac{dN_i^F}{dt} = \left.\frac{\partial N_i^F}{\partial V}\right|_t \frac{dV}{dt} = N_i'$$

This is the amount hitting the membrane per unit time, and if a fraction α_i sticks, then in the differential equations for the activity on the membrane:

$$\frac{dN_{Th}^M}{dt} = \alpha_{Th} N_{Th}' - \lambda_{Th} N_{Th}^M$$

$$\frac{dN_{Ra}^M}{dt} = \alpha_{Ra} N_{Ra}' - \lambda_{Ra} N_{Ra}^M + \delta \lambda_{Th} N_{Th}^M$$

$$\frac{dN_{Pb}^M}{dt} = \alpha_{Pb} N_{Pb}' - \lambda_{Pb} N_{Pb}^M + \epsilon \lambda_{Ra} N_{Ra}^M$$

The parameters δ and ϵ are the respective probabilities that when an atom captured on the surface of the HTiO decays, its daughter is re-captured on the retentate side of the membrane. Any daughters which are not captured are assumed to reach the permeate side, as shown in the equations below. These are, as yet, parameters about which nothing is known, but they are included for completeness.

For the flow in the permeate stream we thus have:

$$\frac{dN_{Th}^P}{dt} = (1 - \alpha_{Th}) N_{Th}'$$

$$\frac{dN^P_{Ra}}{dt} = (1-\alpha_{Ra})N'_{Ra} + (1-\delta)\lambda_{Th}N^M_{Th}$$

$$\frac{dN^P_{Pb}}{dt} = (1-\alpha_{Pb})N'_{Pb} + (1-\epsilon)\lambda_{Ra}N^M_{Ra}$$

Solving the equations for the membrane activity and assuming that the membrane is clean of activity at t=0 gives:

$$\lambda_{Th}N^M_{Th} = \alpha_{Th}N'_{Th}(1-e^{-\lambda_{Th}t})$$

So,

$$\frac{dN^M_{Ra}}{dt} = \alpha_{Ra}N'_{Ra} - \lambda_{Ra}N^M_{Ra} + \delta\alpha_{Th}N'_{Th}(1-e^{-\lambda_{Th}t})$$

The exact solution is thus

$$\lambda_{Ra}N^M_{Ra} = (\alpha_{Ra}N'_{Ra} + \delta\alpha_{Th}N'_{Th})(1-e^{-\lambda_{Ra}t}) + \frac{\lambda_{Ra}\delta\alpha_{Th}N'_{Th}}{\lambda_{Ra}-\lambda_{Th}}(e^{-\lambda_{Ra}t} - e^{-\lambda_{Th}t})$$

If we now consider the permeate side, we have:

$$\frac{dN^P_{Th}}{dt} = (1-\alpha_{Th})N'_{Th}$$

$$\frac{dN^P_{Ra}}{dt} = (1-\alpha_{Ra})N'_{Ra} + (1-\delta)\alpha_{Th}N'_{Th}(1-e^{-\lambda_{Th}t})$$

$$\lambda_{Pb}\frac{dN^P_{Pb}}{dt} = (Z_1 + Z_2 + Z_3)$$

$$Z_1 = (1-\alpha_{Pb})\lambda_{Pb}N'_{Pb}$$

$$Z_2 = (1-\epsilon)\lambda_{Pb}(\alpha_{Ra}N'_{Ra} + \delta\alpha_{Th}N'_{Th})(1-e^{-\lambda_{Ra}t})$$

$$Z_3 = (1-\epsilon)\frac{\lambda_{Ra}\delta\alpha_{Th}N'_{Th}\lambda_{Pb}}{\lambda_{Ra}-\lambda_{Th}}(e^{-\lambda_{Ra}t} - e^{-\lambda_{Th}t})$$

Again, the decays of the atoms on the permeate side are not considered as we are only calculating the activity of small elements of the permeate stream, and not the integrated permeate activity. Now, if we consider the number of atoms, ΔN, which pass a point in the permeate stream between t and t+Δt, then :

$$\lambda_{Pb}\Delta N^P_{Pb} = \Delta t(Z_1 + Z_2 + Z_3)$$

Now, if we also define:

$$A_i = \lambda_i \left.\frac{\partial N_i^F}{\partial V}\right|_t \frac{dV}{dt}$$

Then:

$$Z_1 = (1-\alpha_{Pb})A_{Pb}$$

$$Z_2 = (1-\epsilon)(\alpha_{Ra}\frac{\lambda_{Pb}}{\lambda_{Ra}}A_{Ra} + \delta\alpha_{Th}\frac{\lambda_{Pb}}{\lambda_{Th}}A_{Th})(1-e^{-\lambda_{Ra}t})$$

$$Z_3 = (1-\epsilon)\frac{\lambda_{Pb}}{\lambda_{Th}}A_{Th}\frac{\lambda_{Ra}\delta\alpha_{Th}}{\lambda_{Ra}-\lambda_{Th}}(e^{-\lambda_{Ra}t} - e^{-\lambda_{Th}t})$$

Now, we can simplify this expression by saying:

$$e^{-\lambda_{Th}t} \approx 1 - \lambda_{Th}t + \frac{(\lambda_{Th}t)^2}{2}$$

Thus:

$$Z_3 = A_{Th}(1-\epsilon)\frac{\lambda_{Pb}}{\lambda_{Th}}\frac{\lambda_{Ra}\delta\alpha_{Th}}{\lambda_{Ra}-\lambda_{Th}}(e^{-\lambda_{Ra}t} - 1 + \lambda_{Th}t - \frac{(\lambda_{Th}t)^2}{2})$$

If we also assume that the feed source is in equilibrium so that:

$$A_{Th} = A_{Ra} = A_{Pb} = A_0$$

Then we have:

$$\lambda_{Pb}\frac{\Delta N_{Pb}}{A_0\Delta V} = (1-\alpha_{Pb}) + (1-\epsilon)\frac{\lambda_{Pb}}{\lambda_{Ra}}\left[\alpha_{Ra}(1-e^{-\lambda_{Ra}t}) + \delta\alpha_{Th}(e^{-\lambda_{Ra}t} - (1-\lambda_{Ra}t))\right]$$

where we have said:

$$\frac{\lambda_{Ra}t\lambda_{Th}t}{2} \approx 0$$

$$\lambda_{Ra} - \lambda_{Th} \approx \lambda_{Ra}$$

If we consider the regime where:

$$e^{-\lambda_{Ra}t} \approx 1 - \lambda_{Ra}t$$

Then:

$$\lambda_{Pb}\frac{\Delta N_{Pb}}{A_0\Delta V} = (1-\alpha_{Pb}) + (1-\epsilon)\alpha_{Ra}\lambda_{Pb}t$$

Thus near t=0, the ^{212}Pb DF will be dictated by the chemistry of lead take-up on HTiO, whereas for times of the order of the ^{212}Pb mean life, the DF will tend towards a value dictated by the second term in the above equation. This only becomes a problem if the parameter ϵ is small. This constant is the probability that when a ^{224}Ra atom decays, the ^{212}Pb daughter remains stuck to the HTiO. The problem is that between ^{224}Ra and ^{212}Pb, there is the one minute radon, ^{220}Rn. This is known to be very soluble in water, and also is a noble gas (although it is the 'least noble'). Thus it will not stick to the ion exchanger, and the only process whereby it can remain on the retentate side of the membrane is probably where its recoil momentum is directed into the particle of HTiO on which the ^{224}Ra progenitor is attached. The radon is thus embedded into the HTiO, and its diffusion length is small enough so that the subsequent polonium and lead remain on the inside of the hollow fibre. With a water stream of 1.2 l/min, the probability is that radon introduced into the water on the inside of the fibre will make its way past the membrane before it decays to polonium and subsequently to lead.

This means that we might expect the value of ϵ to be fairly close to zero, and hence the second term in the above equation becomes very important. If infinite DFs are assumed, then the ^{212}Pb DF is purely determined by this second term (as α_i=1), and the lead activity will go from 0 to a value which is directly proportional to the time divided by the ^{212}Pb mean life. For the above experiments this would imply that the lead DF for the three samples would be approximately 100 for the 10l sample, 20 for the 50l sample, and 12 for the 90l sample. As can be seen, this seems to map to the measured values fairly well except for the first sample. This is due to the chemical DF for lead being lower than 100, so that this dominates the activity in the first few minutes. From all this, two conclusions can be drawn: first, that the true lead DF is around 40 after passing 10 litres of water, and secondly that the measurement of lead DFs lower than 15/t, where t is the time of the experiment in hours, is virtually impossible if ^{224}Ra is also present in the feed.

Of course, this is all purely speculative, and depends on the determination of the radon breakthrough parameter, ϵ. It could be that this is actually one, and the lead DF simply falls off with time due to the lead being washed off by water passing over the HTiO. In order to get a better feel for the value of ϵ, another experiment is needed.

Radon flushing experiments

Previous work by the authors had shown that free ^{220}Rn could be obtained from ^{224}Ra on HTiO. A Mediakap 10 (a 150 cm^2 dead end membrane of around 5 ml volume) had 100 ppm of HTiO deposited onto it, and a few hundred Bq of ^{228}Th were pumped past the filter. The filter was gamma counted, and then argon/methane was bubbled through the filter. The gas was wetted by bubbling through high purity water, as the HTiO has a tendency to form a ceramic cake if it dries out. The gas was passed at around 200 cc/min, this being equivalent to approximately 25 bed volumes per minute. The emanation efficiency was found by counting the thallium activity over time.

With such a set-up, emanation efficiencies of around 80% were seen, although the figures varied widely for apparently similar runs. The figure was always above 60% however, and such a high figure gives an indication that the radon breakthrough parameter ϵ could be expected to be a significant factor. In order to test this properly, a new, water-based emanation experiment is needed.

In order to attempt a measurement of the radon flushing, two Mediakap 10's (hereafter referred to as MK10's) were used in a rig shown in figure . Both filters were pumped using the same peristaltic pump drive, onto which two similar size heads were attached. This ensures approximately the same flow rates from the two heads. The pump heads were slightly different in performance however, and the reservoirs were sealed with a slight amount of air in them, so that one reservoir could be over-pressured, while the other was under-pressured. This quickly equilibrates so that the flow rates equalize. Both MK10's were loaded with 0.5 g/m^2 of HTiO, and the flow rate was set at 0.6 l/min. This ensures at least a passing resemblance to the H1 tests above and the 4ft modules proposed for the detector.

The MK10 supplied from the smaller reservoir, MK1, was then run in a separate recirculation rig and around 1 kBq of ^{228}Th was passed over the ion exchanger. The gamma activity was measured and the filter was then inserted into the rig. The idea behind this is that if radon is washed off the first filter, it will spend around 15 minutes in the 9l reservoir before reaching the second MK10. This means that almost all the radon will have decayed to ^{212}Pb by the time it reaches the second filter. Hence, with a disappearance and an appearance measurement, the presence of lead, and not radium or thorium, on the second filter would indicate either radon breakthrough, or lead being washed off the first MK10. These two can be differentiated by removing the 9l reservoir, or its replacement by a much smaller reservoir. If it is radon breakthrough, then the radon will not have time to decay before it sees the second membrane, and thus the second membrane should be clean of activity. Of course, the feeling at this point is for radon breakthrough: if ^{212}Pb was leached off the HTiO, there seems to be no reason why the same should not apply for ^{224}Ra or ^{228}Th.

The first experiment, RF2[5], was done with 10 MΩ water, which is not ideal, as the relatively high ion content means that there is a chance of ^{224}Ra being washed off. Also, the pumping only lasted for around 2 ^{212}Pb half lives. This means that even

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[5] RF = Radon flushing

Sample Name	Litres passed when taken	^{228}Th DF	^{224}Ra DF	^{212}Pb DF
Perm 1	10	>100	>100	120
Perm 2	50	>100	>100	31
Perm 3	90	71	43	14

Table 12: Experiment NS5 - H1MP01-43 membrane - DF measurements.

if the radon breakthrough is 100%, around 25% of the ^{212}Pb will still be left on the first Mediakap, and hence the measured value of ϵ will have an upper limit of 75%. This time limit is imposed by the performance of the peristaltic tubing. This tubing gradually loses its elasticity, and if used continuously, will split.

The results of RF2 are shown in table 13. These show the activities of Bi, Pb, Ra and Th at t=0, where t is measured from the time that the pumping stopped. The activities are given as fractions of the total activity deposited onto MK1 before pumping began. The fitting is done with four exponentials with the decay constants of the four longest lived members of the ^{228}Th chain.

As can be seen, there is a significant difference in the activity levels of the two filters. The first Mediakap, MK1, onto which the ^{228}Th source was deposited, seems to have kept almost 100% of the ^{228}Th, and 60% of the ^{224}Ra. The slight excess in thorium seen at the end is probably due to a slight disequilibria in the feed stock that was put down on MK1. Only around a quarter of the ^{212}Pb is still on the membrane however. On MK2, we have the opposite situation, with an excess of ^{212}Pb, and the ^{212}Bi daughter below lead also. This is important as it shows that either we do have radon flushing, or ^{212}Pb and ^{212}Bi are being washed off preferentially to ^{224}Ra and ^{228}Th. Of course, the ^{224}Ra is washed off to a certain level, but this can probably be attributed to the ion density in the 10l of 10MΩ water being used for this experiment.

In order to proceed, another experiment has to be carried out. This time 18MΩ water was used, and the rig was washed with 0.1M HNO_3 in order to remove any metallic ions in the pipework and reservoirs. The acid was discarded and the system was rinsed to bring the pH back up to 7. The Mediakaps were inserted into the system, and the HTiO was deposited in situ. Again, the deposition of activity was done on a separate rig by recirculating the spike past MK1. This experiment also ran for a much longer time than RF2, namely 61 hours. This equates to around 4 mean lives, and hence leads to an upper limit on the radon breakthrough of 98%.

The activities of the two Mediakaps are shown in table 14.

There are obvious differences between the two experiments. The lead behaviour is obviously in the same direction as RF2, but the effect is somewhat smaller. The

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Figure 2: The two Mediakap system.

main problem is the radium performance. After this discrepancy was first noted, the pH and conductivity of the 10 litres of water was checked. It was found that the previously 18MΩ water was now at pH 5.5, while the conductivity had dropped to 0.2MΩ. This effect is probably due to the saturation of the ultra pure water with atmospheric carbon dioxide. This forms the weak carbonic acid, which would account for the drop in pH. Even though the system was sealed to the air in order to equalize the pump speeds, the air remaining at the top of the reservoirs was not flushed with nitrogen, or any other such precaution.

The slightly acidic nature of the water thus probably elutes off the radium very slowly, and this would explain the fact that less radium was washed off the first experiment, RF2, where the pumping time was that much shorter. As can be seen, a rough equilibrium position seems to have been reached, with the initial radium spike being split half and half between the two membranes. The transport of ^{224}Ra from one Mediakap to the other of course makes the determination of the radon breakthrough that much harder, as now both membranes can emanate radon at a significant level, and hence the amounts of lead and bismuth are functions of the radium activity on both membranes.

A new experiment, RF5, was thus carried out. This time, a gear pump was used to drive the water across both Mediakaps in order to obviate any time limits imposed by the peristaltic tubing, while the redundant 1 litre reservoir was removed. The 10 litre reservoir was thus kept at atmospheric pressure, with an air filter to remove any airborne contamination. The other major change was that the water used in the system was made up to pH10 by the addition of Aristar sodium hydroxide. This ensured that the water was buffered with respect to the absorbtion of atmospheric carbon dioxide.

Filter	^{212}Bi activity at t=0, %	^{212}Pb activity at t=0, %	^{224}Ra activity at t=0, %	^{228}Th activity at t=0, %
MK1	31	24	63	113
MK2	62	76	29	1

Table 13: The first radon flushing experiment - RF2

Due to the high impedance of the two Mediakaps, a flow rate of only around 0.3 litres per minute was achievable, and hence the test was not obviously representative of the flow rates per metre squared used previously. Also, the water being at pH10 can leave us open to accusations of non-applicability, but the only other option was a carbon dioxide removal process which was deemed too overcomplicated for these basically qualitative tests.

The water was pumped for around 45 hours; this is equivalent to around 5% in ^{212}Pbterms (i.e. if all the radon came off the previously loaded Mediakap, there would still be 5% of the lead left on it after 45 hours). The filters were counted after being extracted from the system and the time spectra fitted with four characteristic exponentials. The results are shown in table 15.

As can be seen from the results, the experiment seems to have done fairly well. Again, there is a significant disequilibrium of lead and bismuth, while the radium and thorium do not seem to have been washed off to any significant extent. If the figures are studied, it can be seen that there is also a deficit in the total of lead and bismuth. This could be attributed to either plating on the metal gear pump or flow meter, or that there is a fair amount of radon still contained within the 10 litre reservoir when pumping was stopped. Having said this, it is more probably a combination of the two, and if another experiment were deemed necessary, a sample of the reservoir could be taken for counting also.

Although it smacks of stopping when the right result is obtained, this final radon flushing experiment does seem to give us the expected behaviour. The radon loss parameter seems to be around 75%, or to put it more succinctly, 3 out of every 4 radon atoms produced on the retentate side of the membrane find their way through to the permeate side.

Another possible explanation is that lead and bismuth are being washed off, whereas radium and thorium are not. Again, this is a little hard to believe, as most of the other processes seem to show that lead and thorium follow each other fairly closely on other respects.

Having said this, it would seem that some fairly important conclusions can be taken from this experiment

- Firstly, the problem of falling radium DF's might not be due to ion content as first suspected, but may be due to falling pH as carbon dioxide dissolves in the process volume. This is a tentative conclusion, and seems slightly at odds with previous results, and it may be that a combination of ion content and falling pH both contribute to a decrease in radium DF. Having said this, the use of a metal gear pump in this experiment means that the ion content of such a known interfering species as iron could have been fairly high. This debate is however fairly academic in nature: the D_2O should have neither carbon dioxide or too many metal ions dissolved in it, and we would thus expect the radium DF to hold up in such a situation.

- Secondly, although the flow rate was only around 0.3 l/min, this does correspond to around 100 bed volumes per minute (BVM) for these MK10's. We would expect the radon breakthrough parameter to increase with increasing flow rate per metre squared, but it will obviously top out to some maximum value. Obviously, if we were to run at only around 1 BVM, then there is a chance that the radon produced on the retentate side of the membrane would decay to lead before being flushed out of the membrane. At very large BVM values, the radon will have only a very small chance of decaying to lead before it is past the membrane. In this circumstance, it is difficult to see that increasing the flow rate from 100 BVM to 200 BVM could possibly make much difference. Thus, it seems that the radon breakthrough parameter is around 75% for these membranes. Of course, in the hollow fibre cartridges, there will be different geometry and flow pattern effects, and the extrapolation of this result to a 4 ft membrane seems a little cavalier.

- Finally, it would appear that there are no obvious fines problems with the HTiO in this experiment. The pore size of these MK10's is 0.2 microns, which is at least twice the size of any of the proposed hollow fibre cartridges, and hence any fines problem would be more pronounced in these runs. The signature for fines is that we see an appearance of all the radioactive species as the titanium breaks up and takes the activity with it. As is demonstrated by the holding of the radium and thorium in RF5, there appears to be no such distribution of activity. However, it is important at this point to issue the following caveat: that this experiment was run with the water stream at pH10, which could influence greatly the break up of the titanium. This was anticipated in the decision to take the process volume up in pH, but the only other solution, as stated before, involved the use of carbon dioxide exclusion techniques which were beyond the scope of these experiments. It was deemed much more important to look at the fines problem in a more representative experiment, as detailed below.

Further Work

Obviously, we have raised some interesting points with respect to the removal of radionuclides even at the one foot membrane level. In order to progress further, a new rig has been built, and is shown in figure ??. This system is essentially two cascaded H1 systems, much like those in figure . The difference is that the system is now supplied by a system of ion exchangers designed to give ultra-pure water. In order to do away with the tanks, and hence increase the process volume, this water has to be spiked with a pH7 ^{228}Th source. To get around the problems of plating and source disequilibrium, samples of the feed and both permeates are taken off lines attached to the plumbing. From these, 12ml is removed for direct mixing into scintillation sources. The removal of the upper limit on process volume should allow the investigation of such properties as ^{224}Ra DF reduction, and also allow the first determination of fines from a 0.1μ pore size membrane: the second membrane will catch any HTiO particles smaller than 100nm, but larger than 5nm. An excess of titanium on the second membrane together with a corresponding loss from the first membrane will hence signify that particulate HTiO is washed off. Such a determination can be made either by a direct measurement of the total titanium on the membrane, or an increase of the extraction efficiency of the second membrane, with a corresponding drop in efficiency of the first.

Another experiment that can be done is much like the radon flushing experiment above. This time, the first membrane is coated with HTiO, and then a large spike is circulated past it. The system is then run at 1.2 l/min for as long as is necessary, and any removal of ^{228}Th or ^{224}Ra by the flow of water can be measured by the activity on the second membrane. If a holding tank is introduced between the two membranes, radon flushing can also be investigated.

This double membrane system is basically a concatenation of the two H1 systems used above. Each membrane has a recirculation system much like that used in the NS experiments. Due to the difficulty of adjusting two pumps to run at exactly the same speed, the second pump is used purely for recirculation, while the pump in the first rig provides a high enough pressure to drive both membranes at 1.2 l/min. The three stages of water purification provide a constant stream of $18\mathrm{M}\Omega$ water at anything up to 5 litres per minute. The feed doping adds around 1 ml per minute to this water stream, and the spike is mixed in a reservoir not shown in the diagram.

Filter	^{212}Bi activity at t=0, %	^{212}Pb activity at t=0, %	^{224}Ra activity at t=0, %	^{228}Th activity at t=0, %
MK1	44	41	47	108
MK2	59	64	52	7

Table 14: The results of the second radon flushing experiment, RF3.

Filter	^{212}Bi activity at t=0, %	^{212}Pb activity at t=0, %	^{224}Ra activity at t=0, %	^{228}Th activity at t=0, %
MK1	27	17	98	96
MK2	45	54	4	4

Table 15: The results of the third radon flushing experiment, RF5.

Preliminary Results from DM2 as at 15/3/95

The first experiment with this membrane, DM2, where DM stands for double membrane, began on 20/2/95. The system was set up with an MP01 and P30 in series, both of which had 0.5 g/m^2 deposited on them, and the flow rate was set to 1 l/min. The system was run for around 4 days, this being equivalent to around 5 tonnes of water going past the membranes. If this is scaled to the detector system, this is roughly equivalent to 1 kilo tonne. Samples of the feed and both permeates were taken after 15 minutes, 6 hours and 53 hours, i.e. a total of 9 samples. The membranes were eluted with nitric acid in order to avoid any problems due to the hydrochloric-associated blocking of the membranes.

The activities of the samples are shown in table ??, while the DF's, in are table ??.

In the table we show the log-likelihood fitted activities in units of counts per hour. The DF values are 'per membrane', so that the DF associated with the MP01 is shown in the P1 row, while the DF for the P30 is shown in the P2 row.

So, we can draw some tentative conclusions from these numbers and the elution samples, which are not shown here:

- There appears to be no obvious fines problem. This is established by the amount of titanium eluted off both membranes. The total titanium mass recovered for both membranes is around 90%, while the other 10% is expected to be still on the membranes, although a 10% dissolution of titanium is not excluded.

- There were large disequilibria problems with the feed stock, as can be seen in the activities of the F1 samples. This was attributed to plating in the feed stock bottle, but these differences obviously calibrate out in the DF determination.

- The DF's for the MP01 appear fairly good, especially for the thorium. Again, the lead DF is affected by radon breakthrough, and a tentative conclusion seems to be that the radon breakthrough parameter is of the order of 60%. The radium DF is fairly inconclusive, although the cumulative DF for the two membranes is very good. The low radium DF for the MP01 is not easily explained, but it could be a combination of pH and ion saturation problems. This is to be investigated more closely in the next experiment, where the feed stock is going to be set at ph 7, rather than ph 4, as in DM2.
- The membrane performance, in terms of dead end flow rate against trans-membrane pressure, seems not to have been adversely affected by the run, with recirculation cleaning bringing both back to within a few tens of percent of their respective initial values. This demonstrates the problem with HCl elution even more forcefully, and much work has to be done on just what happens during HCl elution that causes such drastic reductions in membrane characteristics.

As said before, these results are preliminary, but the experiment has already been upgraded by fitting a 10 litre reservoir between the two membranes. This tank has already been independently tested to 7.5 bar, and hence the single pump will be able to pressurize it to the correct value to drive 1 l/min across the second membrane. This reservoir should allow enough time for radon to decay, and a large excess of lead on the second membrane will again confirm the prejudice for radon breakthrough. These experiments should be started in April, and will hopefully give demonstrable improvements in the extraction of lead.