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The Removal of ^{234}Th from NaCl solution

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1. INTRODUCTION

Working with thorium in solution, especially at higher pH values, can pose many problems due to the thorium precipitating and plating out. As well as investigating the effectiveness of various methods of removing thorium from NaCl solution, we gained an insight into the behaviour of thorium at these pH levels. This report is the result of a four week undergraduate project undertaken by S. Lilley under the supervision of M. Omari and E. W. Hooper.

2. EXPERIMENTAL PROCEDURE

In all our solutions we used ^{234}Th solution as a tracer in NaCl. To obtain a measure of the concentration of thorium present, a Ge-Li gamma detector was used to give the counts in 1000s of the 92.6keV line in the thorium spectrum. The standard measure used throughout the project was counts per 1000s per 50ml.

For each experiment, a solution of thorium was prepared from uranyl nitrate by first ether extraction¹ and then dissolving in 9M HCl and passing through an ion-anion exchange column. The effluent was then brought to the required pH by the addition of NaOH. At this stage, high-purity NaCl was added as required by the particular experiment, and the solution left to equilibrate overnight.

To treat samples of this solution with a given adsorber, the solution was transferred to a glass flask and the adsorber added. This was then placed in a reciprocating shaker bath for 1 hour at 25°C and at a shaking speed constant for all experiments. Further procedures were specific for given experiments.

2.1 Experiment 1

Using 250ml of solution at pH7 with a NaCl concentration of 5.2% (by weight) and a specific activity (SA) of 13660 ks^{-1} , five 50ml samples were treated as above: four with different adsorbers ($\text{Fe}(\text{OH})_3$, Sb_2O_5 , HTiO and MnO_2) at 100ppm (metal ion concentration, by weight) and one left as a control. After this, each sample was centrifuged for 3 minutes and the supernate transferred to a 50ml polystyrene vessel and counted. The control was also counted before centrifuging.

2.2 Experiment 2

Using 200ml of solution at pH7 with 5wt% NaCl and a specific activity of 34000 ks^{-1} , 100ml was treated with HTiO at 100ppm Ti and 100ml was treated as a control. The control was passed through an Amicon ultrafiltration rig resulting in 50ml of permeate being collected together with 50ml of concentrate. Both these were counted. The rig was then rinsed using 0.1M HCl and deionised water. A 50ml sample of the rinse water permeated through the filter was counted to give an idea of the background. The procedure was the repeated with the Ti treated solution.

2.3 Experiment 3

Using solution at pH7 with 5.5% NaCl and a SA of 23000 ks^{-1} , exp. 2 was repeated but using the Carbosep UF rig instead of the Amicon. In addition, this rig was cleaned with 3M HNO_3 and before each run, a dummy solution of 5wt% NaCl was filtered, collected and counted for the background.

2.4 Experiment 4

A one litre solution was made up at pH7 with 5wt% NaCl and a total activity of around 140000 ks^{-1} . This was then filtered using a funnel with a glass fibre plug. The plug was soaked in conc. HCl which was then diluted to 50ml and counted.

The solution was then passed through the Carbosep UF rig, having counted 50ml which was returned. 18x50ml samples of permeate were collected in order to

observe a saturation curve for the filter. The remaining 100ml of concentrate was also counted.

2.5 Experiment 5

Two old solutions of similar activity, pH7 and 10wt% NaCl were recounted. They were then both filtered using Nalgene syringe microfilters with a pore size of 0.2 μ m, and the permeates counted. The second solution was refiltered with a clean filter and counted. In addition, one empty bottle was filled with deionised water and counted.

2.6 Experiment 6

Using 150ml of solution at pH7, 5wt% NaCl and SA of 40000 ks⁻¹, three 50ml samples were treated as for the adsorbers except two samples had different sized pieces of the Carboxep membrane placed in them and one was treated as a control. After the one hour contact time, the solutions were decanted into bottles and counted.

For this and further experiments, precautions were taken to keep the level of dust and fibres in the solutions as low as possible. This was achieved using glass fibre filters at all stages before neutralisation.

2.7 Experiment 7

Before neutralising the thorium in HCl, the solution was passed through the ion exchange column a further two times, in order to significantly reduce the level of residual uranium. The acid was then brought to pH5. A sample of this solution was removed and the rest was brought to pH7.

50ml samples of these two solutions were then counted, microfiltered as in exp. 5, and recounted.

2.8 Experiment 8

Using the pH7 solution mentioned in exp. 7, three 50ml samples were taken. One was treated with a piece of Nalgene microfilter element, one with a piece of activated charcoal and the other as a control, using the shaker bath for 1 hour. The counts before and after were taken.

2.9 Experiment 9

Using samples prepared from the solutions mentioned in exp.7, the following adsorption tests were made, with appropriate controls. At pH5: HTiO at 10,40 and 100ppmTi. At 10ppmTi; pH 3,4,5 and 6. To do these, the samples were treated as in exp. 1, but after centrifuging, the supernatant liquor was microfiltered (0.2 μ m). For the run at pH6, the solution used was the permeate from a microfiltered solution.

3. RESULTS

The standard measure for the effectiveness of an adsorber is the decontamination factor (DF). This is defined as.

$$DF = ({}^{234}\text{Th activity before process}) / ({}^{234}\text{Th activity after process})$$

The activity before was taken as the activity of the control, unless otherwise stated. Another measure used was the relative adsorption, or the fraction of the total activity adsorbed. This is simply $1-(DF^{-1})$.

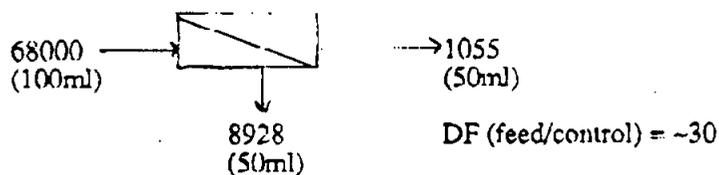
3.1 Experiment 1

	SA (ks^{-1})	DF(Typical error ~15%)
Feed Solution	13660	-
Control before centrifuging	12300	-
Control after centrifuging	7150	-
Adsorbers; Sb	133	53
Ti	117	63
(100ppm) Fe	60	119
Mn	134	53

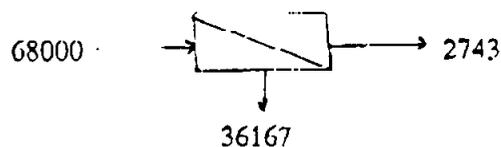
3.2 Experiment 2

(Background = $\sim 30ks^{-1}$ for both runs)

Control (figures are total activity):



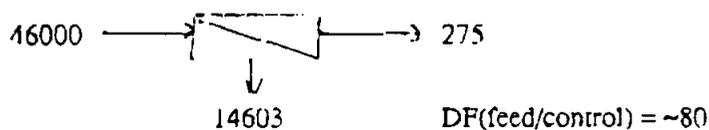
Ti @ 100ppm:



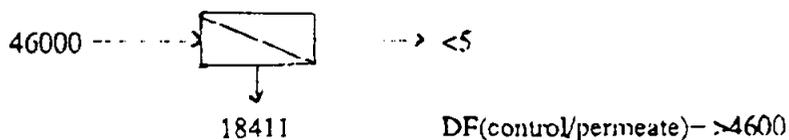
3.3 Experiment 3

(Background = $\sim 5 ks^{-1}$)

Control;



Ti @ 100ppm



3.4 Experiment 4

Activity on plug filter = $\sim 65000 \text{ ks}^{-1}$ (therefore a DF of ~ 2)

The samples of permeate (all 18) registered at around the background level of 10 ks^{-1} . The total activity of the concentrate was found to be 10000 ks^{-1} . 50000 ks^{-1} was recovered from the membrane upon rinsing with conc. HNO_3 .

3.5 Experiment 5

(Figures given are activities in ks^{-1})
1st. solution;

16000 \longrightarrow μ filter \longrightarrow 500
 \downarrow
 700 (Empty bottle) DF = ~ 30

2nd solution;

19358 \longrightarrow μ filter \longrightarrow 610 \longrightarrow μ filter \longrightarrow 556
 DF = ~ 30

3.6 Experiment 6

Feed Soln...	$\sim 40000 \text{ ks}^{-1}$	(All at 6% NaCl)
Control	36732 ks^{-1}	
Small portion	36300 ks^{-1}) No appreciable reduction given the experimental error of $\sim 5\%$.
Large portion	36100 ks^{-1}	

3.7 Experiment 7

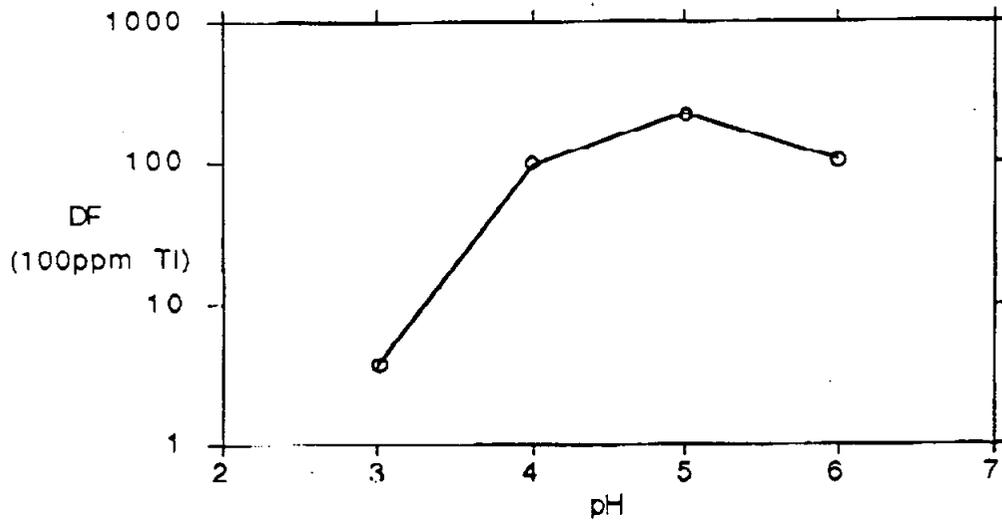
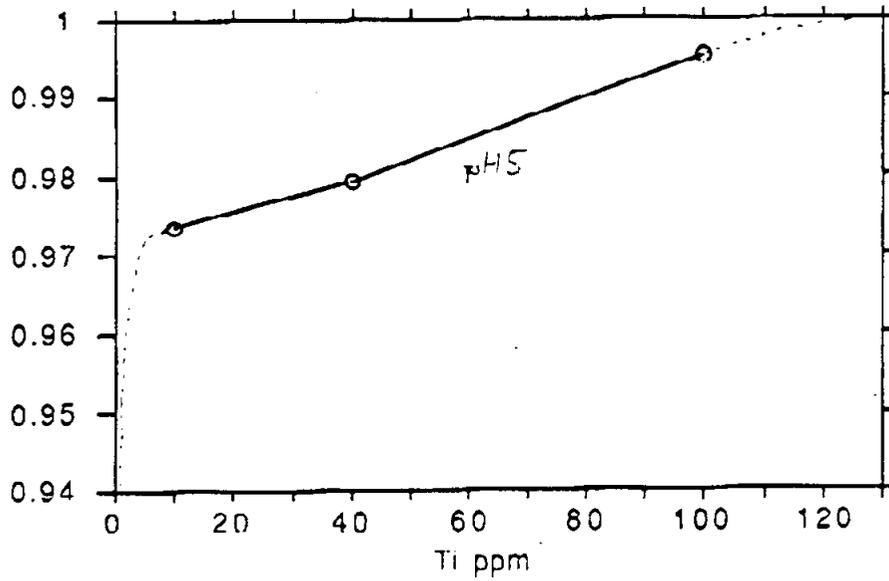
pH5; (10% NaCl)	30800 ks^{-1}	\longrightarrow μ Filter	\longrightarrow 30380 ks^{-1}	
	feed		permeate	
pH7; (6% NaCl)	19156 ks^{-1}	\longrightarrow μ filter	\longrightarrow 740 ks^{-1}	DF = ~ 25

3.8 Experiment 8

Feed Solution	19156 ks^{-1}
Control	17415 ks^{-1}
Filter Membrane	18647 ks^{-1}
Charcoal	17266 ks^{-1} (All counts $\pm 1.5\%$)

Exp. 9

Rel. Adsorption



4. ANALYSIS

From experiment 1, it was apparent that $\text{Fe}(\text{OH})_3$ was the best adsorber for thorium, but HTiO was chosen for further investigation due to its effectiveness in sorbing radium and problems with introducing Fe into the water system. The result from exp. 3 using the Amicon filter was somewhat spurious, later to be explained when cleaning the system. A large amount of activity was found on the prefilter, some of which may have been released during the backwashing procedure.

The large DFs obtained by just filtering the feed solution (exp 4) may be explained either by the membrane adsorbing the thorium itself, or something being filtered out with the thorium attached to it. Experiments 5 and 6 suggested that the membranes were not adsorbing the thorium and, indeed, there was something in solution.

The alternatives were either that there were fibres or uranium precipitate in solution which adsorbed most thorium and were later filtered out or that the thorium itself formed large complexes that were filtered out. When the fibre and dust content was reduced and the uranium concentration taken down, there was no change in DF (Exp. 7) suggesting that there was some large thorium complexes present. At pH5 evidence suggested that these large complexes were not present. More evidence for this theory was provided in the results for experiment 8.

The DFs at varying pH obtained in experiment 9 can perhaps be explained by the combination of two factors; the lowering of adsorber efficiency and the increase in colloidal particle size with rising pH. It would be interesting to repeat this experiment with a smaller pore size filter such as the Carbosep UF rig. Unfortunately, time ran out before this could be realised.

Outside saturation levels, the relative adsorption ought to be fairly linear with adsorber concentration, which appears to be the case. Of course in saturation levels, it is also linear, but with a much higher slope. To find the cutoff for saturation, more results need to be obtained for low levels of Ti. It appears from the graph that the highest DF values at pH5 will be for Ti concentrations of around 130ppm. A suggestion would also be to try at other contact times apart from 1 hour in order to get the 'full picture'.

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REFERENCE

1. A. Alian, M. Khaliqzaman, M.M. Nofal, J. Radioanal. Nucl. Chem. Letters 108 /5/ 317-326 /1986/