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An initial investigation of the absorption of thorium from 10% salt solution.

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1. Introduction.

Following the recent confirmation that the intended additive to the heavy water in SNO for neutral current signal detection was to be high-purity sodium chloride, methods of purification now require further investigation. It is believed that salt with a thorium content around 1 ppb can be obtained from commercial sources, but this content would need to be reduced by about three orders of magnitude, to around 1 ppt, before the salt could be used in the SNO detector. Other elements, particularly radium, uranium and lead, are also of interest but this report only deals with thorium.

Although other methods have been suggested, the most practicable method of purification seems at present to be to dissolve the salt in either light or heavy water and attempt to remove the thorium with a suitable absorber. Use of light water implies a later drying stage but allows a wider choice of methods. If heavy water can be used a drying stage can be avoided. A possible technique is seeded ultrafiltration using fine-grained absorbers. This technique is being studied for monitoring purposes as well for initial purification of salt as supplied. Another technique is to pass the salt solution through a column or packed bed of absorber, which then needs to be in the form of coarser-grained granules or beads. A variation on this technique is a filter pre-impregnated with an absorber as used by Crespo et al. (1). Other possible methods involve the addition of a chelating compound to the solution, followed perhaps by nanofiltration or by adsorption of the chelate on C18-coated silica or similar material. The work reported here was intended as a brief investigation of the granule or bead type absorbers immediately available and also as an exercise to develop the experimental protocols for further work.

2. Previous work and the chemistry of thorium.

Previous work by Ferraris (2) is relevant, and includes a large number of useful references. It was mainly concerned with extraction of radium and thorium from pure water by Seakem beads, of which more later, as a function of pH and flow-rate. However in one experiment (FLOW9) he found that at neutral pH the presence of 0.25% NaCl seemed to enhance the adsorption of thorium (but not radium) by this material. The other discipline with most interest in extracting thorium from salt solution is oceanography, and most information available from that source is naturally for sea-water. This can be compared to a 3 w% salt solution at about pH 8 but it contains other ions. However the speciation of Th in 0.422 M NaCl solution as a function of pH has been discussed by Hunter et al. (3) who reported absorption measurements on iron oxide and manganese dioxide. Their figure 6 is particularly instructive. At low pH (2 or less) thorium is expected to be present either as the fully ionised species Th++++ or as (ThCl)+++. At high pH (6 or more) thorium is expected to be entirely in the form of the fully hydrolysed species Th(OH)4 which is uncharged, although its polymers may not be. The interesting region is in-between, where species with a charge of 3, 2 or 1 may also be present.

At neutral pH it is generally believed that absorption, changes in speciation or restoration of equilibrium following any disturbance are all slow processes with time constants of minutes, tens of minutes or even hours. This does not matter much in the sea, which has got plenty of time. However at lower pH kinetics should be faster. At the same time the Kd or equilibrium distribution coefficient may well be reduced as the solution is made more acid. It might then be anticipated that for any particular combination of absorber form, column dimensions, flow-rate and salt concentration there could be an optimum pH for maximum absorption. During normal operation of SNO there is very little scope for changing the pH from neutral, but the initial purification of salt could easily be done at whatever pH gave best results. As long as acidification is done with HCl and any subsequent neutralisation done with NaOH the only net result is to slightly increase the total amount of salt.

3. Experimental procedures.

All the tests were carried out using 10 w% NaCl solution, made by dissolving 100 g of ICI vacuum-dried salt in 900 ml of D.I. water. The pH adjustments were made by adding Analar grade HCl or NaOH solutions of similar strength. Prepared solution was stored in a 1 litre PVC Nalgene bottle, spiked with Th-234 and adjusted to the desired pH. Similar but unspiked solution was used for conditioning absorbers before testing.

The Th-234 used as tracer was extracted from U-238 in the form of uranyl nitrate hexahydrate (UNH) by dissolving 10 g of UNH in diethyl ether, using the method reported by Alian et al. (4), which left the Th-234 absorbed on a 55 mm diameter filter paper in the bottom of a 150 ml beaker. It was dissolved from the filter paper with 9 M HCl and purified from residual U by passing the solution through a column of anion-exchange resin (5), usually a small column containing Dowex 1-X8(Cl), 18-52 mesh (0.30 - 0.85 mm). A larger column containing Amberlite IRA-400(Cl), 14-52 mesh (0.30 - 1.18 mm) was also available and was used before the small column for some extractions. The eluate was evaporated to small volume and dissolved in a few ml of 1 M HCl. The resins had been conditioned by washing with D.I. water to remove any fines, then with dilute HCl, then with 3 M, then 6 M and finally 9 M HCl. This procedure is claimed not only to avoid the risk of damage to the resin due to osmotic shock but also clean it of any traces of Fe and other contaminants.

Batch contact experiments were done using 100 ml borosilicate glass (Duran) screw-top Erlenmeyer flasks. A weighed quantity of an absorber was placed in the flask and conditioned with salt solution. Then 50 ml of spiked solution was added and the flask was shaken in a water bath for 1 hour at 25 C. In order to ensure complete removal of any suspended fines the supernate should ideally then be centrifuged, but for these tests that step was omitted and 50 ml of supernate was decanted directly into a polystyrene culture flask and its activity counted with a GeLi using the 92.6 keV gamma line. Control samples, using a flask containing no absorber, were also counted.

Small column experiments were done using a glass chromatography column equipped with a Rotaflo stopcock (Quickfit C12/10). The bore was 10 mm and bed depths of 5-6 cm were used, the bed volume (BV) thus being about 4-5 ml. Solution passing through the column was collected in 50 ml polystyrene culture flasks and counted with the GeLi. Some additional experiments were done with similar but larger columns, 18 mm bore.

4. Absorbers available for test.

A number of absorber materials were available. Six small samples of inorganic ion exchangers had been supplied by the French company R.A.N. (Recherche Appliquee du Nord), from their range of over twenty. This company has since been taken over by another French company STMI (Societe des Techniques en Milieu Ionisant) and is now known as STMI - RAN Department. The address is:

STMI, Direction Commerciale,
9 Rue Fernand Leger,
91190 Gif sur Yvette, France.
Tel: 69 07 78 02. Fax: 69 07 70 08. Telex: 600419.

Attention Mr. Bluy, Technical Sales Manager.

The six samples were:
OXTI - Oxide of Titanium,
FERROX - Oxide of Iron,
MANOX A - Oxide of Manganese,
POLYAN M - Polyantimonic acid,
OXTAIN - Oxide of Tin,
ZIROX - Oxide of Zirconium.

They were in the form of granules in the size range 0.1 to 0.5 mm. These materials are not mechanically very strong and there are some limitations on the maximum column depth which can be used. They also require some care in conditioning to avoid bursting. The recommended procedure is first to spread the absorber out in a thin layer on a sheet of plastic and expose it to the atmosphere for at least 24 hours. Then the absorber should be washed to remove fines by decanting, using a solution having the same acidity and composition as the solution to be treated. The recommended contact time to ensure good solution-exchanger equilibrium is 3-4 hours. The absorber should then be suspended in this solution and poured into the column, ensuring that no air bubbles are trapped between the granules.

These materials are also available as fines (less than 0.1 mm), which are intended for batch contact use followed by settling or filtration. They cost about 2000 FF/kg. There is a mention of technical collaboration with UTC (Compiegne University of Technologies) for the further development and testing of these absorbers.

Another material available is called BIRM, or, to give it its full name, Clack's Birm, regular grade. It is a granular filter medium containing catalysed manganese dioxide and is normally used for the removal of dissolved iron or manganese from water supplies. The grain size is 9-35 mesh, the effective size being 0.61 mm. A fine grade is also sold; 14-48 mesh, with an effective size of 0.49 mm. Cost is low, about 4 pounds per kg. It is actually sold by the litre. It had been supplied by Elga Ltd., High Wycombe, UK, but they are not the makers.

One of the concerns is to what extent thorium may be absorbed onto the surface of the acrylic sphere, since it is known that at neutral pH thorium does readily adsorb, or "plate-out", onto surfaces of containers. Two samples of acrylic were available. One was a sample of ICI "Diakon" acrylic powder intended for the production of acrylic mouldings. The other was a sample of Aldrich low-molecular weight PMMA, code 18,223-0. It had been noted earlier by Black (6) that Diakon powder absorbed thorium from water at pH 7. Costs of plastics moulding powders are low, a few pounds per kg.

A number of chelating resins have been developed for extracting multivalent ions from water containing much higher concentrations of monovalent ions. The only material to hand was Amberlite IRC-718, which is a cross-linked macroreticular weakly acidic cation exchange resin with a chelating function, made by Rohm and Haas. It is supplied, as spherical beads, in the fully hydrated sodium form and is claimed to be usable from pH 2 to 14. Size is 16-50 mesh. Cost is about 60 pounds per kg. Adsorbed ions can be readily eluted from the resin by strong acids at pH 1 or less. A number of other chelating resins are made by other manufacturers. For example, Duolite C 467, also made by Rohm and Haas, is claimed to have a high affinity for lead and to be used for purifying brine. Similar resins, Lewatit TP 208 and OC 1060, are made by Bayer AG, Leverkusen.

The other absorber material to hand was the SEAKEM beads with which much earlier work has been done. These are beads of Amberlite XAD-7 macroreticular polymeric acrylic ester which have been coated and impregnated with manganese dioxide by treatment with potassium permanganate solution. (7). This material was developed for research in oceanography and is said to contain at least 5% MnO_2 by weight. For the purposes of SNO this is not necessarily optimum; kinetics may be better with a lower loading. It also contains a significant amount of potassium as supplied and has a strongly alkaline reaction. Cost is fairly high, about 600 pounds per kg.

5. Experimental results.

5.1. Batch contact tests series 1.

For these tests the spiked salt solution was at pH 1.5. Rather small amounts of absorber were used and conditioning was done with only 2 ml of unspiked solution and not very thoroughly. For each material the weight of absorber used and the activity of the decanted supernate as a percentage of that of the control are given in the following table.

Absorber.	Weight.	Activity, %
OXTI	5 mg	95.2
FERROX	5 mg	96.4
MANOX A	5 mg	85.3
POLYAN M	5 mg	93.4
OXTAIN	5 mg	98.7
ZIROX	5 mg	95.4
BIRM	5 mg	95.7
DIAKON	5 mg	94.8
IRC-718	15 mg	92.8
SEAKEM	50 mg	75.3

The IRC-718 resin is supplied moist and is about two-thirds water, hence the dry weight would be about 5 mg as for the other absorbers. The weight of SEAKEM beads used was based on the assumption that the active absorber content was only about a tenth of the total weight. However, because of its macroreticular structure it is "all surface" which makes comparisons a little difficult. The two absorbers which gave most reduction in activity, MANOX A and SEAKEM, are both based on MnO_2 as the active ingredient, but the results may also reflect their high alkalinity if not properly conditioned. The pH of 1.5 at which these tests were done is outside the recommended range for the IRC-718 resin yet some absorption was found, possibly due to pH shift.

5.2. Batch contact tests series 2.

For the second test series the amount of absorber was increased by about a factor of ten and the pH of the spiked solution was brought up to 2.5. Conditioning was again done with 2 ml of unspiked solution. Results are given in the following table.

Absorber.	Weight.	Activity, %	D.F.
OXTI	50 mg	89.1	
FERROX	50 mg	92.6	
MANOX A	50 mg	39.1	2.56
POLYAN M	50 mg	72.6	
OXTAIN	50 mg	96.2	
ZIROX	50 mg	88.4	
BIRM	50 mg	96.5	
LMW-PMMA	50 mg	99.5	
IRC-718	150 mg	45.2	2.21
SEAKEM	250 mg	8.2	12.24

Decontamination factor (D.F.) was only calculated for those cases where the activity of the supernate was less than half of that of the control. LMW-PMMA is the Low Molecular Weight PolyMethyl MethAcrylate (Aldrich), which can be seen to have negligible absorption at pH 2.5. The grain size is coarser than the Diakon powder. Note that the amount of SEAKEM beads had been increased by 5, not 10. The conditioning and pH control was not too good with the increased amount of absorber so this may have affected some of the results. In addition there was some perceptible cloudiness in the supernate from POLYAN M, and some lesser but still detectable cloudiness in the supernate from MANOX A and from FERROX, which could also have affected their results.

5.3. Batch contact tests series 3.

For the third series the pH of the spiked solution was adjusted to 4.4 and the amount of unspiked solution used for conditioning was increased to 10 ml. The amount of absorber used was similar to the second series except for the SEAKEM beads. Results are given below.

Absorber.	Weight.	Activity, %	D.F.	"Equilibrium %"
OXTI	50 mg	76.9		22.3
FERROX	50 mg	88.7		34.4
MANOX A	50 mg	40.8	2.47	13.2
POLYAN M	50 mg	54.5		12.0
OXTAIN	50 mg	78.1		50.9
ZIROX	50 mg	63.5		31.8
BIRM	50 mg	88.2		42.1
LMW-PMMA	50 mg	95.6		91.2
IRC-718	150 mg	68.4		35.9
SEAKEM	50 mg	52.9		16.0

Following the gamma-counting of the supernates they were put back into their glass flasks and allowed to contact the absorbers for a further period of over 24 hours. This should give an approximation to equilibrium. 50 ml of supernate was then again taken and counted and the results are in the last column above. The differences between the two sets of figures are considerable and confirm that at pH 4.4 at least it does take several hours to reach equilibrium.

5.4. Small column tests.

a) IRC-718.

3 g of moist IRC-718 resin was washed with D.I. water and then conditioned in 10% salt solution. The pH was repeatedly adjusted to 3.5 by adding drops of HCl solution until it remained stable. It was then transferred to the column where it formed a bed 10 mm diameter and 52 mm deep. Spiked salt solution was passed through the column at a flow rate of

5-10 ml/min and collected in 50 ml polystyrene flasks. These were counted and their activity compared with 50 ml of the feed. The results are given below. Bed volume was calculated to be 4.1 ml.

Sample no.	Activity, %.	D.F.
1	26.6	3.75
2	28.1	3.55
3	27.7	3.61
4	27.7	3.60
5	24.4	4.10
6	22.0	4.54
	Mean	3.83

b) BIRM.

3.1 g of BIRM was washed in D.I. water and then immersed in 10% salt solution. The pH was adjusted to 3.5 by adding HCl until it was stable, then the material was transferred to the column. Bed depth was about 60 mm. Spiked salt solution was passed through the column, the first 50 ml sample slowly, taking 16 minutes, and the second rather faster, taking 6 minutes. They were counted and compared with a sample of the feed. Results are given below.

Sample no.	Activity, %.	D.F.
1	49.1	2.03
2	49.3	2.03

c) SEAKEM.

1.5 g of SEAKEM beads were washed in D.I. water, then conditioned in 10% salt solution to pH 3.5 and loaded into the column. Bed depth was 62 mm. Spiked salt solution was passed through, the first sample in 15 minutes, the second in 10 minutes and the third in 5 minutes, all times being approximate. They were counted and compared with a sample of the feed. Results are given below.

Sample no.	Activity, %.	D.F.
1	7.0	14.12
2	18.9	5.30
3	16.3	6.13

5.5. Larger column tests.

As none of the small column tests had a particularly low flow rate, expressed as BV/hr, they would not be likely to have sufficient contact time to yield a good D.F. The bed depth would also be much too shallow. Two tests were therefore done with larger columns.

a). BIRM.

BIRM was chosen for this test on the grounds that it is cheap, we [illegible]d plenty of it and it gave the lowest D.F. of the three materials used [illegible] the small column tests; thus if a good D.F. could be achieved with this material the others should be satisfactory also -- hopefully, with proper optimisation of pH, considerably better.

40 g of BIRM was washed in D.I. water and conditioned in 10% salt

solution to pH 3 by adding HCl. This was repeated until the pH remained above 4 for a long time. It was adjusted to pH 3.6 and loaded into an 18 mm diameter column. Bed depth was 208 mm, giving a BV of 52.9 ml. Spiked 10% salt solution at pH 3.4 was passed through the column and collected in 50 ml flasks. Three samples were taken at low flow-rate and one at high flow-rate. They were counted and compared with the activity of a control sample. Results are given below.

Sample no.	Time to collect.	Flow-rate in BV/hr.	Remaining activity, %.	D.F.
1	11 min.	5	3.1	32.2
2	8 min.	7	0.0	>100
3	7 min.	8	0.0	>100
4	70 sec.	56	10.2	9.8

The activity in sample 1 is probably due to a small trace of fines which can be seen in it. Although it was thought that the bed had been washed clear of fines it seems this was not so. All the later samples were clear.

b). IRC-718.

10 g of IRC-718 moist resin was washed in D.I. water (initial pH of the wash water was about 10) and conditioned in salt solution to pH 3.5. It was loaded into an 18 mm diameter column, but the bed depth was only 54 mm and it was difficult to obtain a slow flow-rate. Spiked solution at pH 3.4 was passed, but there was evidence of break-through and the data are not good enough to report. At moderate flow-rates around 20 BV/hr a D.F. of about 10 seems indicated, whereas at a very high flow-rate of about 180 BV/hr the D.F. observed was only 1.8. Further experiments are needed. Work reported by Riley and Taylor (8) and by Luttrell et al. (9) using another chelating resin, Chelex-100 (Bio-Rad), strongly suggests that better absorption would be obtained at a higher pH value, in the range 5.0 - 7.6, and that flow-rate should not exceed 5-6 BV/hr. Although Blount et al. (10) suggested operating at a pH of 2.0 - 2.5 for the absorption of those elements which hydrolyse at higher pH it would seem that Kd may be too low at this pH.

One attractive feature of chelating resins is that the adsorbed polyvalent metals can be fairly readily eluted with acid. For IRC-718 resin 4-15% hydrochloric or sulphuric acids are suggested. However it was found that passing 50 ml of 1M HCl through this column was sufficient to give good recovery of the absorbed Th-234.

6. Discussion.

None of the batch contact results should be regarded as being conclusive at this stage because of some doubts over pH control and fines, but it is clear that significant adsorption of thorium from 10% salt solution can be achieved by suitable adjustment of pH and that some absorbers seem to be better than others. The experimental difficulties which may be encountered are now fairly well understood. For any method of initial purification of salt which involved dissolving in light water there could be some advantages in operating at higher concentration than 10% if this is possible, since the salt must be dried again before it can be added to the heavy water, and therefore tests at a salt content of 25% with selected absorbers are suggested. Kd is expected to decrease approximately inversely with the square root of ionic strength (9). For most tests except those in the first series the weight ratio of solution to absorber was about 1000:1 and this seems to be a convenient ratio to use in future tests. Kd values were not calculated, but could be from the raw data given, taking the control activity as equal to the feed. In most of the tests a D.F. significantly greater than 2 implies a Kd of at least 1000. Spiking levels varied for different tests but were a few Bq/ml. The thorium concentration which would give an activity of 1 ddt (disintegration per day per tonne) if present as Th-232 will give 2.5 Bq/ml if present as Th-234.

The small column tests were done at flow rates which correspond to between about 40 and about 100 BV/hr, whereas normal commercial operation of absorber columns is rarely done at more than 10 BV/hr, i.e. an order of magnitude less. A minimum bed depth of 600 or 700 mm is also normally recommended for absorber columns, i.e. an order of magnitude more than used in these tests. It therefore seemed likely that any absorber/pH combination which showed a significant D.F. in these tests would be effective in removing thorium from salt solution if used with more conventional column parameters, although further tests were clearly necessary. It was noticed that a slower flow-rate seemed to give an appreciably better D.F. with the SEAKEM beads but that no difference was found with the BIRM granules, possibly reflecting the fact that the one has a macroreticular (highly porous) structure into which the solution takes time to diffuse while the other does not. Future tests should be done at lower flow-rates.

The larger column test using BIRM gave data suggesting complete thorium removal for low flow-rates, less than 10 BV/hr, and at a pH of about 3.5, but which, because of the statistical errors of the gamma-counting, can only be reported as a D.F. of at least 100. It should be noted that this is a material which is not sold as, nor intended as, an absorber in the usual sense and is not normally operated below pH 6.8. While further tests are needed, using other absorbers and at a range of pH values, this data does suggest that the desired D.F. of 1000 should be achievable with an optimised column process. So far the process parameters of absorber material, flow-rate and pH have only been investigated in a rather preliminary and cursory fashion, and the salt concentration and temperature have not been varied at all. There are some more general considerations too. Bed depth must be adequate if a high D.F. is required and the aspect ratio of the bed should be as high as reasonable practicable; the effective capacity of a given volume of absorber before break-through occurs varies as the square root of bed depth. In fact the large number of possible process parameter combinations is one of the reasons for this report being written at this point; discussions are desirable on how best to proceed. The main reason is of course to have it available before the next water meeting.

While for this application it is desirable to use an absorber which is readily commercially available, it should be noted that many different chelating resins have been reported in the literature and that a resin with a higher selectivity for thorium from brine could probably be made if needed. Both IRC-718 and Chelex-100 are believed to be iminodiacetic acid type and thus selective for divalent over monovalent cations. It has been confirmed (11) that polyvalent cations are absorbed on a one-per-site basis irrespective of valency. Therefore, for trivalent or tetravalent cations more ligands per adsorption site might be expected to give higher stability and selectivity. For example, Marhol and Cheng (12) prepared 12 new resins by adding another ligand to a resin of this type and tested them on a number of cations. One of them, Resin IX, had a Kd of over 21,000 for absorption of Th from 0.25M ammonium acetate solution at pH 3.5. Moyers and Fritz (13) went one better by preparing a propylenediaminetetraacetic acid resin with four COOH ligands per site. As expected, this PDTA-4 resin had high selectivity for Th and Zr from hydrochloric acid solutions and was also found to have good selectivity for U and Cu. In practice the absorbers available seem likely to be adequate.

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