

Plate-out of ^{228}Th , ^{224}Ra and ^{212}Pb onto
 PP, Acrylic and Hastelloy in UPW and EDTA solutions
 M. Shatkay, I. Bleviss

* with collaboration of W. Locke, Oxford, UK

September 1994

During the July 1994 SNO water group meeting the issue of plate-out of radioactive species on the surfaces of the SNO detector water system was raised. Such plate-out has the potential to foul the background monitoring systems as unmonitored Th which plates out will give rise to Rn. This Rn in turn can migrate in the system, decay to a 10.5 hrs lead which may reach the detector and give there rise to 2.6 MeV gamma rays. A subsequent problem is the plate out of lead on parts of the system prior to the background monitoring system, interfering with the lead monitoring scheme (Laberge et al., 1994) which is our only path for sampling unsupported Rn in the system.

The following bench top experiment was proposed (July 1994) and carried out in parallel at Oxford and at CRPP: coupons machined of the various materials encountered in the heavy water system were immersed in the following solutions:

Ultra Pure Water (UPW, 18 M Ω)

1 ppb EDTA solution

100 ppb EDTA solution

0.2% MgCl₂ solution

0.2% MgCl₂ solution with 1 ppb EDTA

0.2% MgCl₂ solution with 100 ppb EDTA

All solutions were made with UPW and in duplicate. The solutions were titrated to pH 7 (the expected pH of the detector), spiked with TH 228 solution in equilibrium with its daughters and the coupons were then immersed in these solutions for 24 hours (no mechanical agitation provided). After this time the coupons were counted in an alpha counter. The solutions were transferred to a new container and both old and new containers were gamma counted in order to monitor adsorbed activity on the plastic surface of the bottle.

EXPERIMENTAL:

1) Coupons: 27x47x3 mm³ (surface area of 30 cm²) coupons were cut out of PP, Acrylic and Hastelloy (designated in the following tables as PP, Acr, Has). The first two materials were cut out of 1/8" sheets (STC, Carleton U). The hastelloy coupons were cut out of a C-22 Hastelloy pipe of the same stock as to be used in SNO (K. Mcfarlane). The pipe was flattened and than cut into coupons. A total of 25 coupons of each material were machined. The coupons were washed by sonicating 2 hours in a 5% Radiacwash solution, rinsing in hot water and then in UPW. Th activity on two sample coupons following cleaning is included in table

1. 8 coupons of each material were sent to Oxford, England. These were used for the experiments involving $MgCl_2$ solutions. The ones left in CRPP were used for the UPW solutions. One overlapping experiment was allowed so as to compare the systematics of the two labs. For the Oxford group this was the UPW+100 ppb EDTA run. For the CRPP this was the 0.2% $MgCl_2$ +100 ppb EDTA run.

2) Reagents: Milli Q Plus (Millipore) water (UPW);
 $MgCl_2$ salt anhydrous (BDH) weighed in a dry glove box, made into a 5% solution;
EDTA as the tetra sodium salt (BDH) at 30 ppm and 0.5 ppm;
Th 228 spike made in 1 N HNO_3 at a concentration of ≈ 2000 Bq/cc. 30 μ litres of spike (≈ 60 Bq) were added to each sample;
NaOH (Anachemia) 2.2×10^{-3} M (used for titrations);
 HNO_3 70% Anachemia reagent grade (diluted to 1N);
125 cc PP wide mouth bottles (Nalgene) prewashed in Radiacwash, 10% HNO_3 and UPW. These are molded of homopolymer PP with no release agents.

3) Preparation of solutions: 100 microlitres of 30 ppm EDTA for the 100 ppb solutions and 60 microlitres of 0.5 ppm EDTA for the 1 ppb solutions were first pipetted into the bottles. 1.2 cc of $MgCl_2$ were added when necessary. The volume was made up to 1.25 cc in all bottles by adding UPW. Then 30 microlitres of 1N HNO_3 were added followed by 30 microlitres of the Th spike. The contents were mixed manually for a few minutes and then titrated to pH 7 by the addition of 28-29 cc NaOH solution, to a total volume of 30 cc. pH meter used was Fisher Accumet 915 with a Fisher mercuric chloride glass electrode. The resulting pH was determined to be 6.85 ± 0.1 .

4) Plate-out experiment: coupons were placed in the solutions so that $\approx 15cm^2$ of the total coupon surface (50%) is immersed. The wetted surface area in the PP bottle was estimated to be 30 cm^2 /bottle. 24 hours later the coupons were drawn out and rinsed by 5 cc UPW. This 5 cc was collected and added to the holding bottles. The coupons were dabbed gently with kimwipe to remove water from surfaces not to be counted. The upper surface was dried by gently blowing clean air from a canister along it from the non immersed portion towards the immersed portion. The coupons were then transferred to the alpha counter. The spiked solutions were placed in a second set of bottles, the first set were further rinsed with 5 cc UPW and this rinse water added to the second set. Both sets of bottles were then gamma counted in order to assess the Pb plate-out on the PP walls. Several of these bottles were also counted 10 days later in order to assess Th plate-out.

5) Counting: Counting of coupons was performed by a dual chamber Ortec alpha counter 16 channel NIM-PC DAQ with a $1.5cm^2$ surface silicon detector. Walls effectively colimate the the signal so that the counted area is also $1.5cm^2$. Geometrical efficiency is $<50\%$ due to the walls (estimated at 30% by G. Laberege). Counting time was ≈ 1 hour/pair, to a total of 4 hours. Some of the coupons were re-counted a week later to confirm reproducibility of the counting procedures. In all cases the Th peaks were equal (to within $\leq 20\%$). Standards were prepared

by evaporating 2 microlitre of spike solution ($\approx 4\text{Bq } ^{28}\text{Th}$ in equilibrium with its daughters) on each of the tested material planchette (PP, Acr, Has) in the form of a drop at the center of the counted area, and counting the respective alphas.

Gamma counting was carried out by centering the 125 cc bottles in front of a germanium gamma counter and counting at 239 KeV (^{212}Pb) for 30-60 minutes immediately following the experiment. The short time allowed for counting (30 min.) resulted in extremely large errors for the first set of bottles, with an average value of 250 ± 200 cph out of a total measured activity of 3500 ± 700 cph. The different location of the activity in the two sets of bottles (walls in the first, solution in the second) would further result in a different geometrical efficiency. That said, the results are in agreement with previous results deduced from stable lead, where 30 cc lead solutions placed in pp vials of 15 cm^2 surface area lost $\leq 20\%$ of the lead onto the walls.

RESULTS:

Effect of coupon material:

The alpha counting data are presented in table 1. The different materials exhibit markedly different behaviour. ^{228}Th and ^{224}Ra plate most on Hastelloy and least on Acrylic. ^{212}Pb plates on PP and Hastelloy to the same degree (in UP-W). Acrylic seems to be the least prone to plate out exhibiting activities of 1-10 times the background activity. The Th activity measured on 1.5 cm^2 Hastelloy is equivalent to 6.7% of the total activity in the solution (see table 1, spikes section). Correcting for the total area immersed in the solution (15 cm^2) it is concluded that 70% (!) of the total Th spike plated out on the Hastelloy coupons. A similar calculation indicates that 20% of the total lead spike have plated out on the Hastelloy. An equivalent amount of Pb have plated out on PP coupons in UPW.

Further difference between the materials is exhibited by the Rn/Ra data (table 1) where PP appears to emanate Rn within the chamber (at 100 millitorre) while no loss of Rn is indicated from Hastelloy. One would thus assume that Th plated out onto PP pipes in the SNO water system will indeed give rise to mobile Rn, and the subsequent lead would travel further in the system, necessitating its monitoring and extraction.

The above estimate of lead plate out onto PP may be used to estimate the Pb plate out onto the 30 cm^2 surface of the PP bottles. A fraction equivalent to 40% of the total spike is calculated, in disagreement (at the 1 sigma level) with above quoted gamma counting measurements. In order to avoid different counting geometries, future tests will be conducted where cut surfaces of PP bottles will be directly counted by alpha counting.

Effect of EDTA

Pb plate out is reduced by 3-7 in the presence of 100 ppb EDTA. A smaller reduction (x2-6) is observed in Acrylic. No effect on Hastelloy is observed.

The effect of EDTA varies for the various isotopes and materials: a small (x2-3) reduction in Th plate out on PP is evidenced at the 100 ppb level. The presence

of $MgCl_2$ does not interfere with this reduction. EDTA does not prevent plate out of Th onto Hastelloy and only marginally reduced it on Acrylic.

Ra plate out is not affected by the presence of EDTA. See also Appendix. The poor performance of EDTA in preventing plate out onto Hastelloy might be tied to the metallic behaviour of Hastelloy in aqueous solution. Two coupons were sent to UBC (C. Whalthingam) in order to measure leaching of metallic ions from Hastelloy. If such leaching takes place, the metal ions might compete with the radioactive species for EDTA. Conversely the metal surface might have a higher affinity to the radioactive species than the EDTA, and furthermore, EDTA-M complexes are known to be preferentially adsorbed onto certain surfaces (e.g. SiO_2 , Al_2O_3 , Bowers and Huang, J. Coll. Interf. Chem., 110, 1986).

While the results indicate plate out of activity may be of concern in the SNO water system (where PP is the major component and some large Hastelloy surfaces are exposed), several issues are not addressed by the above set of tests.

- The plate out on membranes, comprising the largest surface area in the system, has not yet been investigated
- The kinetic effects (flow, residence time etc.) have not been varied and would be difficult to simulate
- Temperature is an important variable, as adsorption increases with decrease in temperature
- The nature of the exposed surface (machining, copolymer vs. homopolymer in PP, etc.) might play a role in its adsorptive behaviour.

FUTURE EXPERIMENTS:

1) The dependence of the EDTA effect on its concentration at the very low radioisotope levels suggests that the results may reflect kinetic processes. The experiment will therefore be repeated for PP and Hastelloy as before, but with a mechanical agitation insuring perfect mixing of the plating solutions throughout the experiment duration (24 hours). Such agitation could be provided by an orbital shaker. Temperature may be controlled at 10 C.

2) Titration procedures will be modified in order to simulate better conditions in the SNO detector, and avoid irreversible formation of hydrolyzed species during the addition of concentrated (0.0022M) NaOH solution. Instead, a 2 μ litre Th spike (1 μ Ci/cc) in 0.1N HNO_3 will be used and diluted to 30 cc UPW (resulting in a pH > 5). NaOH of pH 8 may then be added to reach neutrality.

3) Stripping of plated-out Th and Ra activity by 100 ppb EDTA solutions is to be studied. Removal of plated out Pb will be studied using stable lead (since the duration of the experiment may exceed $2 \times T_{1/2}$ of ^{212}Pb).

4) Large scale plate-out experiment using PP pipe of 50 L (?) (previously used by H. Lee to measure Rn emanation) and a solution flow of 20 LPM is planned (E. Bonvin). Th plate out will be assessed by Rn emanation. Stable lead may be added to the spike and plated-out lead may then be removed by acid and analysed

Table 1 - Activities (cps) measured on coupons

Conditions: 24 hrs, no agitation, \sim 60 Bq solution,
1.5 square cm area counted of a total
immersed area of 15 square cm (*)

Spikes and background:

Background of blank, precleaned, planchettes (measured for PP and Acrylic):

Th	Ra	Pb
0.0005 pm 0.0003	0.003 pm 0.002	0.003 pm 0.002

6.7% of total spike on plachettes:

pp (Th)	acr (Th)
1.68	1.40

(i.e. 90 Bq spike)

Th 228

Sample	[edta] (ppb)			
	0	1	100	100Mg
pp1	.1	.05	.05	.03
pp2	.07	.15	.02	.03
pp1 LT	.1	.05	.05	.03
acr1	.02	.02	.02	.01
acr2	.10	.03	.008	.05
acr1 LT	.02	.02	.016	.014
has1	1.	1.4	1.5	1.2
has2	1.2	1.0	1.3	1.2

"pp" = polypropylene
 "acr" = acrylic
 "has" = hastealloy
 "Mg" = MgCl2 0.2%
 "LT" = counting performed 7 days after the experiment

Ra 224

Sample	[edta] (ppb)			
	0	1	100	100Mg
pp1	.04	.05	.06	.006
pp2	.02	.02	.04	.008
acr1	.009	.007	.007	.002
acr2	.015	.015	.04	.01

has1		.12	.22	0.25	0.14
has2		.18	.16	.28	.15

Pb-212 (\$)

=====

correction for decay before counting.

Sample		[edta] (ppb)			
		0	1	100	100Mg
pp1		.60	.8	.09	.08
pp2		.53	.2	.14	.19
acr1		.14	.06	.006	.006
acr2		.09	.05	.02	.19
has1		.55	.72	.41	.70
has2		.62	.54	.41	.51

(\$) This is unsupported lead (Po), counted 0-4 hours from the time of its deposition, corrected for the 0.64 branching ratio.
 Ra 224 ingrowth (based on above Ra 224 data) was always less than 10% of measured lead activity.

:

Ra/Rn (#)

=====

Sample		[edta] (ppb)			
		0	1	100	100Mg
pp1		4	2.5	2	3
pp2		1.5	1.7	1.3	2
pp1 LT		2	2	2	2
acr1		1	2	1	2
acr2		1	2	2	1
acr1 LT		1	2	1	1
has1		1	1	1	1
has2		1	1	1	1

(#) Rn is supported in the counting chamber by Ra 224.
 Excess Ra indicates loss of Rn from the coupon, and subsequently from the chamber.

(*) 5% variability between two chambers was not corrected for in the above data.

Appendix- Pb/Ra/Th plate out test on pp vial with/without EDTA

Three clean 30ml pp vials (Nalgene) were randomly picked to carry out a plate out test on the walls of pp vials. One vial was filled with ultra-pure water and the other two were filled with 100 ppb EDTA solution prepared on two different days. About 100 bq of Th228 source was spiked in each vial. The pH of the three solutions were all measured to be 4.0 pm 0.2. Counting was performed on a gamma counter at 239 KeV (Pb212) as described above. The initial counts were taken within three hours of the spike.

After an overnight period of time (21 hour) the contents of these three vials were transferred into another set of vials. The first set of empty vials were rinsed with UPW then filled with UPW and put back to count. Counts were recorded periodically, and the plated out Pb, Ra and Th were calculated accordingly as a fraction of the original activity.

21 days (500 hours) later, the contents in the second set of vials were emptied. Vials were rinsed with UPW and filled with UPW. Counts were taken periodically to check plated out activity of Pb, Ra and Th in these vials.

Results:

Results are reported in table 3.

The 24 hours contact time vials indicate 4-8 % plate out of the three isotopes on the walls in UPW. No activity was detected for the 100 ppb EDTA treatment.

With the contact time increased to 21 days (second set of empty of vials), the amount of Ra and Th retained on the UPW vial increased to 26 percent and 76 percent respectively. The amount of Pb plated out was only 8 percent. This last result is suspect since the vials were not tightly sealed throughout the 21 day duration of the experiment. 30% loss of Rn was observed from solutions under similar conditions in 21 days.

Thus the actual amount of lead plated on the walls may be 12% or higher.

No activity was observed in the two 100 ppb EDTA vials clearly suggesting that the EDTA prevents the Pb, Ra and Th from sticking onto the pp vial walls.

Table 3

Contact time (hours)	EDTA (ppb)	Pb	Ra (% of spike)	Th
24	0	6.2	4.2	7.6
	100	nd	nd	nd
500	0	8.2(*)	26	76
	100	nd	nd	nd

(*) Rn loss during experiment.