Characterisation of NORM Contaminated Objects: Reliable & Efficient (CONCORE)

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Center for Nuclear Technologies

Objectives of CONCORE

- Experimental section dealing with the basic investigations required to evaluate factors affecting characterization measurements.
- Review of existing methods to perform initial characterization of NORM contaminated equipment .

Origin of the problem – scale formation

- *Formation water* is the often hyper saline water in the oil reservoir
- *Produced water* is a mixture of formation water and sea water.

Ion species	Formation water, ppm	Seawater, ppm
Na	31275	10890
K	654	460
Mg	379	1368
Ba	269	0
Sr	771	0
SO_4^{2-}	0	2960
Cl-	60412	19766
Ca	5038	428

Barium in produced water

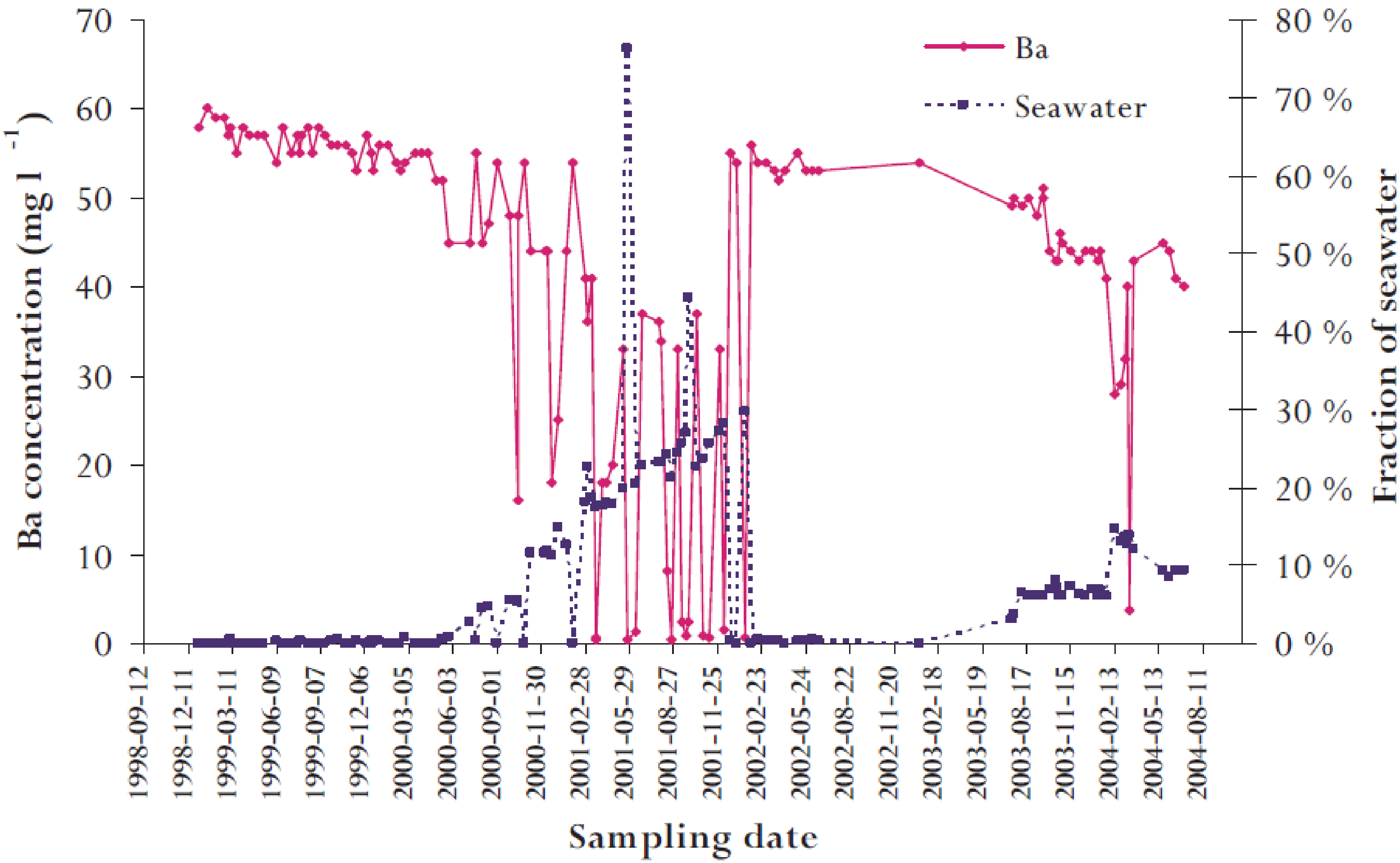


Figure 3.1. *Concentration of Ba and seawater fraction in produced water at Statfjord Nord (unpublished data from Thingvoll, Statoil, 2004).*

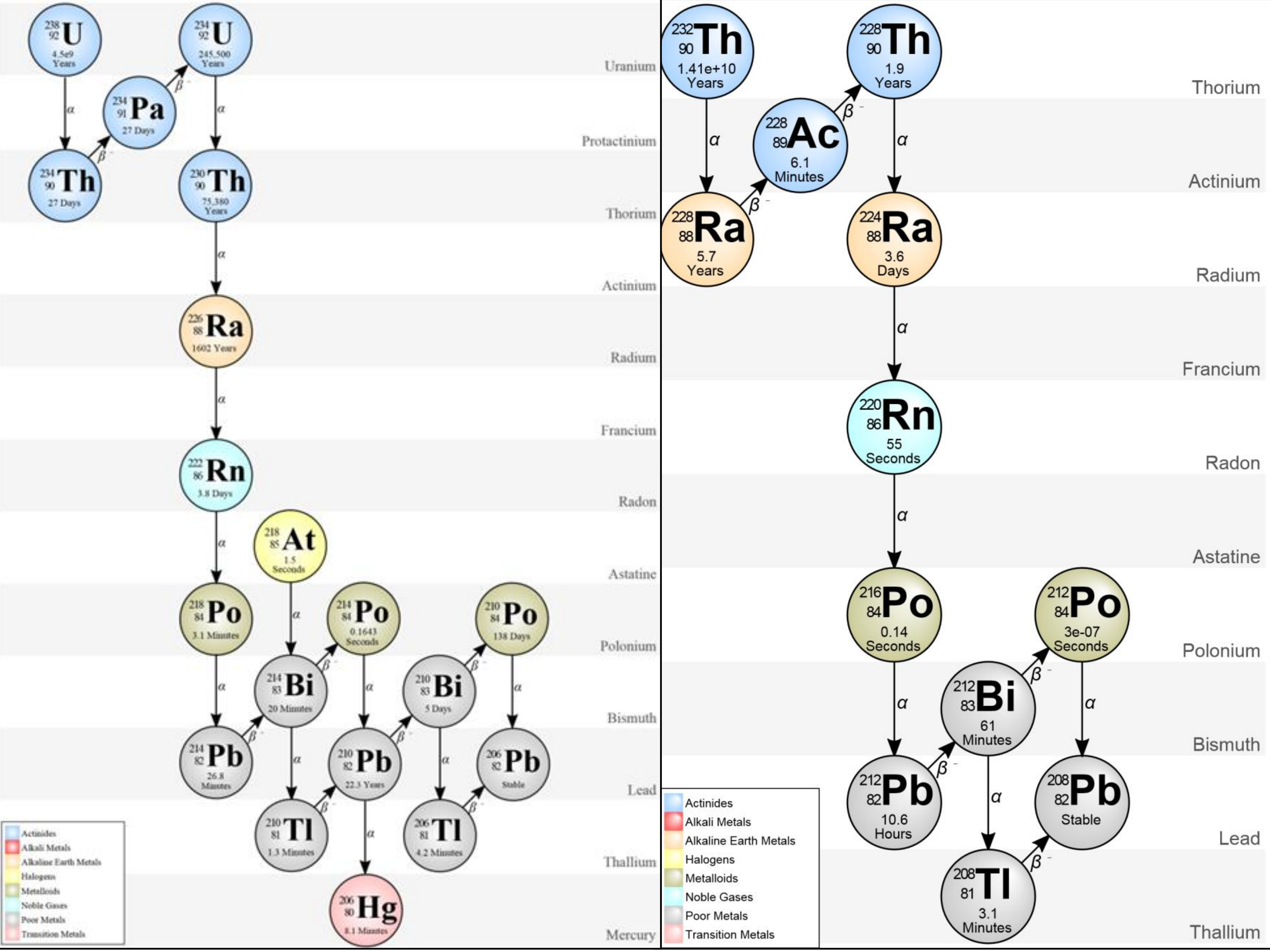
Periodic Table of the Elements

Atomic Number
Symbol
Name
Atomic Mass

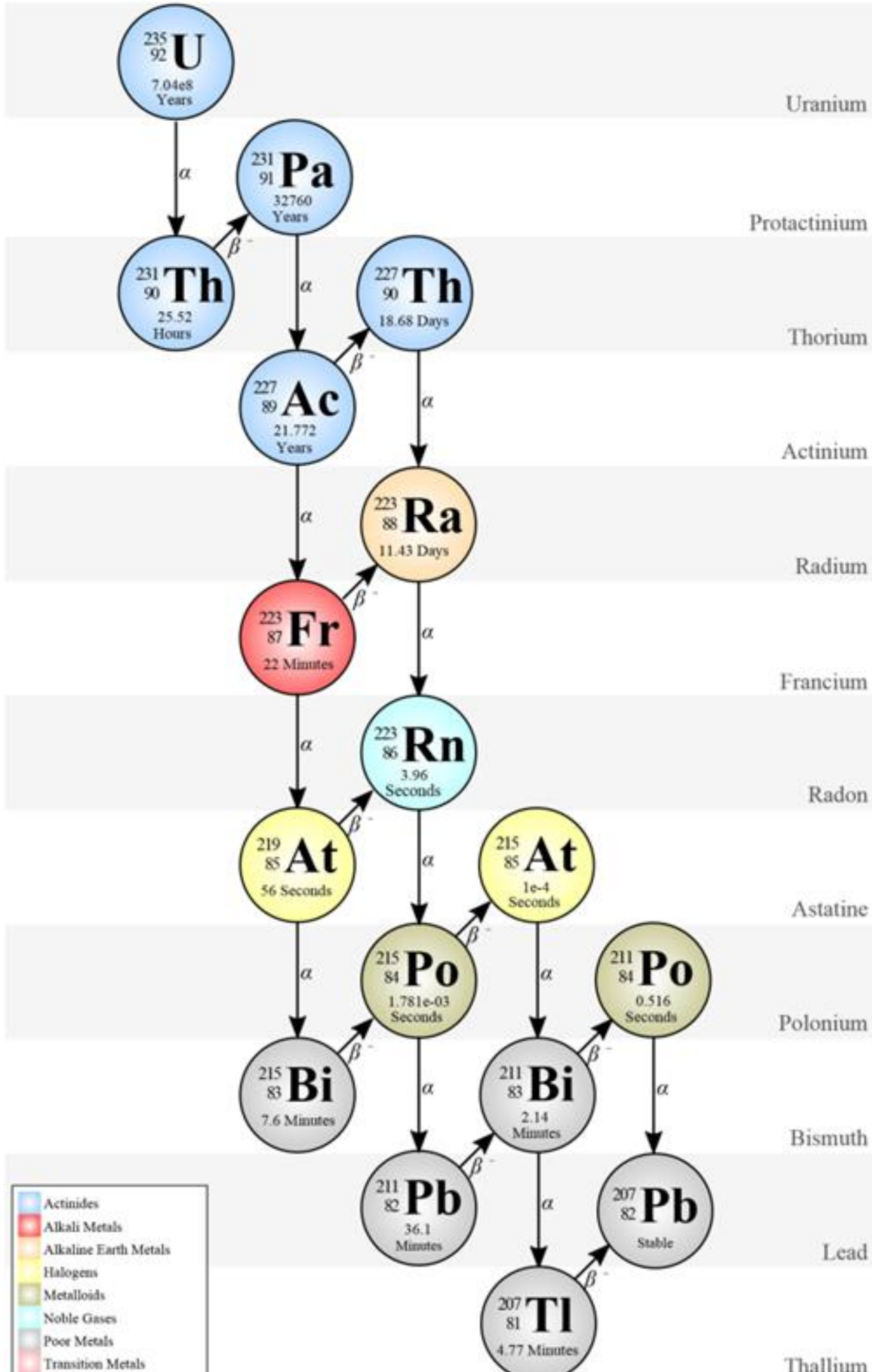
1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 84.798
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Semimetal | Nonmetal | Halogen | Noble Gas | Lanthanide | Actinide



238 92 U 4.5e9 Years
234 91 Pa 27 Days
234 92 U 245,500 Years
234 90 Th 27 Days
230 90 Th 75,380 Years
226 88 Ra 1602 Years
222 86 Rn 3.8 Days
218 85 At 1.5 Seconds
218 84 Po 3.1 Minutes
214 84 Po 0.1643 Seconds
210 84 Po 138 Days
214 83 Bi 20 Minutes
210 83 Bi 5 Days
214 82 Pb 26.8 Minutes
210 82 Pb 22.3 Years
206 82 Pb Stable
210 81 Tl 1.3 Minutes
206 81 Tl 4.2 Minutes
206 80 Hg 8.1 Minutes
α
β⁻
Uranium
Protactinium
Thorium
Actinium
Radium
Francium
Radon
Astatine
Polonium
Bismuth
Lead
Thallium
Mercury
Actinides
Alkali Metals
Alkaline Earth Metals
Halogens
Metalloids
Noble Gases
Poor Metals
Transition Metals
232 90 Th 1.41e+10 Years
228 90 Th 1.9 Years
228 89 Ac 6.1 Minutes
228 88 Ra 5.7 Years
224 88 Ra 3.6 Days
220 86 Rn 55 Seconds
216 84 Po 0.14 Seconds
212 84 Po 3e-07 Seconds
212 83 Bi 61 Minutes
212 82 Pb 10.6 Hours
208 82 Pb Stable
208 81 Tl 3.1 Minutes
Thorium
Actinium
Radium
Francium
Radon
Astatine
Polonium
Bismuth
Lead
Thallium
Actinides
Alkali Metals
Alkaline Earth Metals
Halogens
Metalloids
Noble Gases
Poor Metals
Transition Metals


235 92 U 7.04e8 Years
Uranium
α
231 91 Pa 32760 Years
Protactinium
β⁻
231 90 Th 25.52 Hours
α
227 90 Th 18.68 Days
Thorium
β⁻
227 89 Ac 21.772 Years
α
Actinium
α
223 88 Ra 11.43 Days
Radium
β⁻
223 87 Fr 22 Minutes
α
Francium
α
223 86 Rn 3.96 Seconds
Radon
β⁻
219 85 At 56 Seconds
α
215 85 At 1e-4 Seconds
Astatine
β⁻
α
215 84 Po 1.781e-03 Seconds
α
211 84 Po 0.516 Seconds
Polonium
β⁻
215 83 Bi 7.6 Minutes
α
211 83 Bi 2.14 Minutes
β⁻
α
Bismuth
β⁻
211 82 Pb 36.1 Minutes
α
207 82 Pb Stable
Lead
β⁻
207 81 Tl 4.77 Minutes
Thallium
Actinides
Alkali Metals
Alkaline Earth Metals
Halogens
Metalloids
Noble Gases
Poor Metals
Transition Metals

The present problem

- Need to replace or clean tubulars when scale deposits are too heavy.

- Classification of NORM contamination done at sea using hand instruments. Repeated measurements at shore may show different values.

- Identification of contaminated material based on the 1Bq/g limit using dose rate or contamination monitors.

- Different procedures are being used for categorization of NORM by the operators in the North Sea.

1 - Experimental part of CONCORE

Possible reasons for observed difference in readings between offshore and onshore measurements.

- Variation in water content of tubes.
- Decay or build-up of short-lived radioisotopes.
- Different measurement techniques (instrument, operation, distance).
- Loss of loss of radon
- Etc…

→ The main task of the experimental part was to try and find out if any of these parameters may explain the variable results often found.

Toys for the present project

Donated by Mærsk Oil & gas

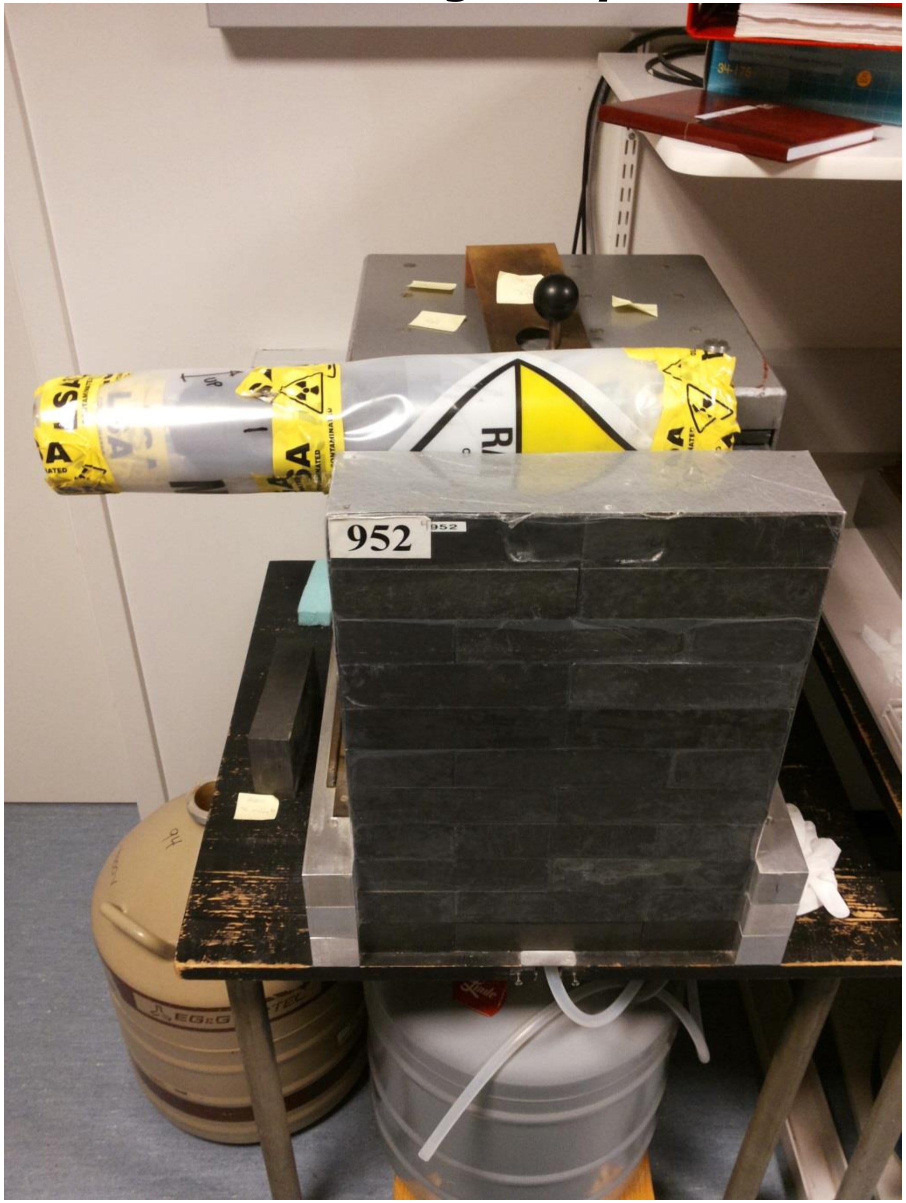
DTU

Explosives used in the early days to remove loose scale in tubulars !

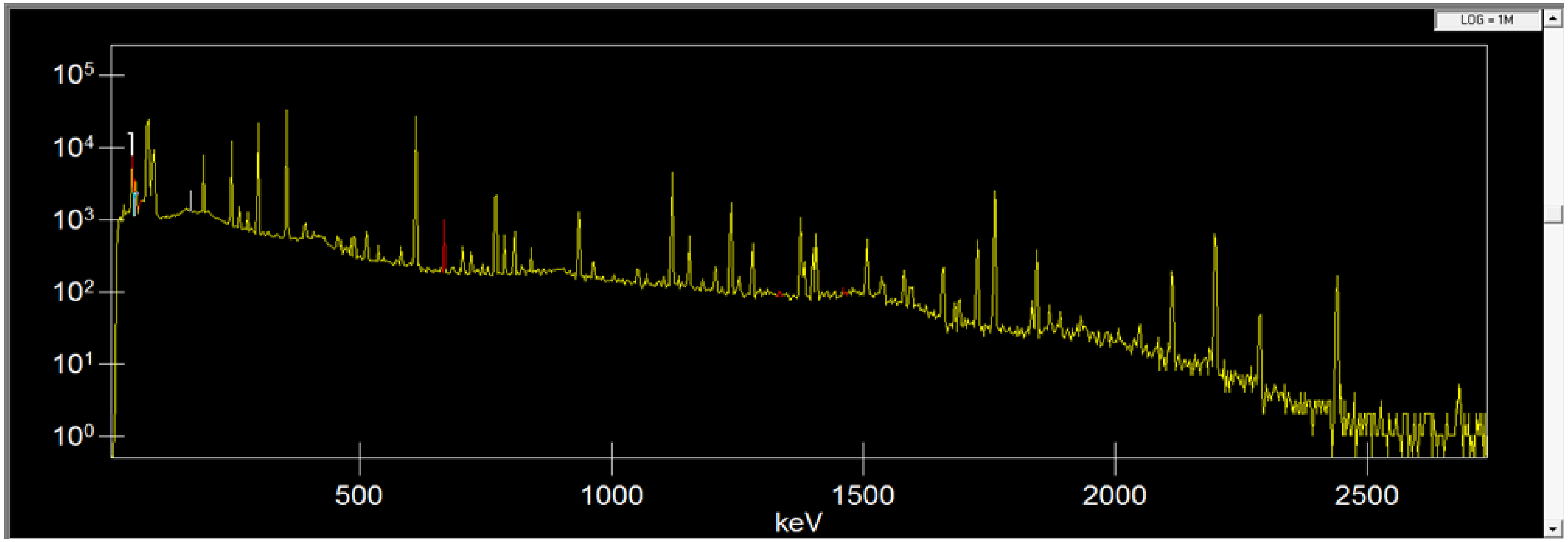
A sledge hammer worked well too!


TUBE - 2

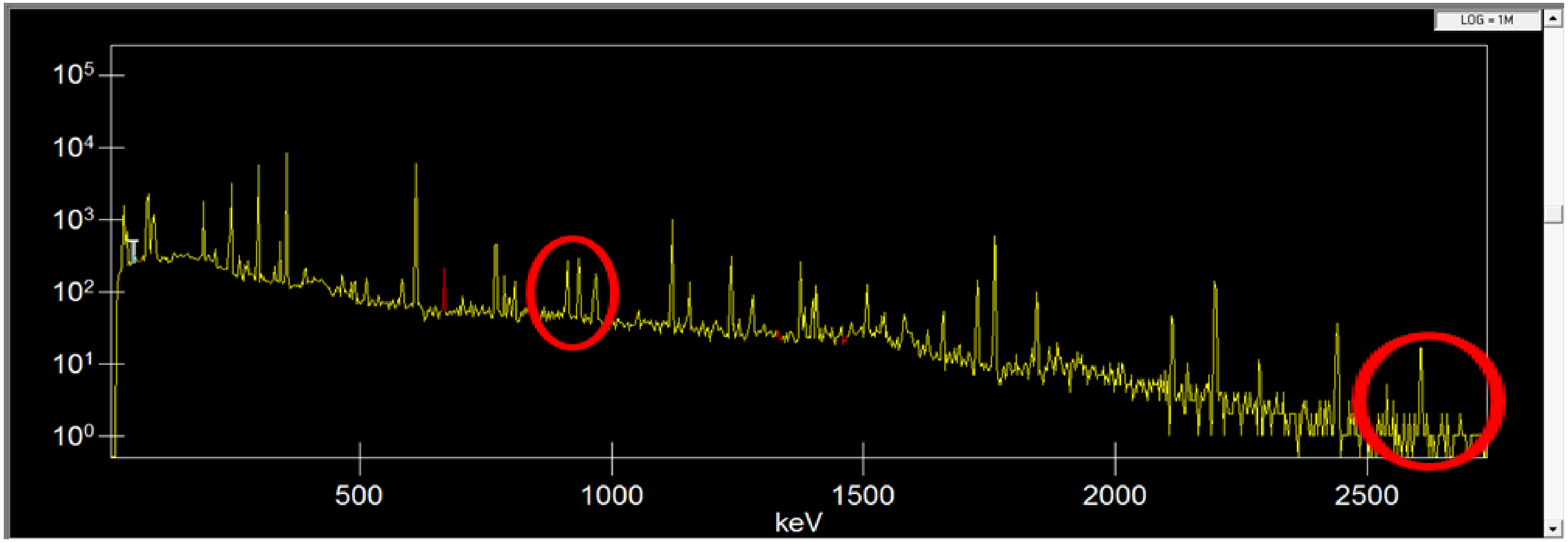
Inhomogeneity?



Major gamma contribution from scale is from Ra-226 - daughters



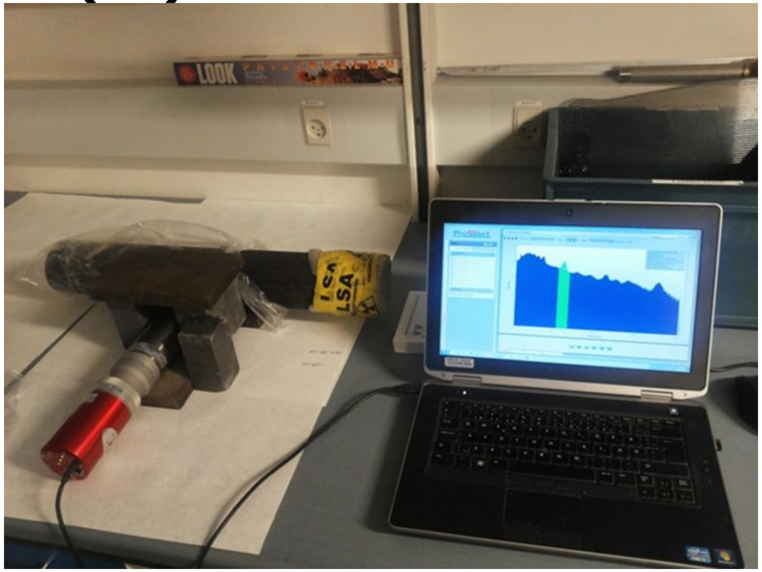
Ra-226 + daughters in equilibrium from standard source



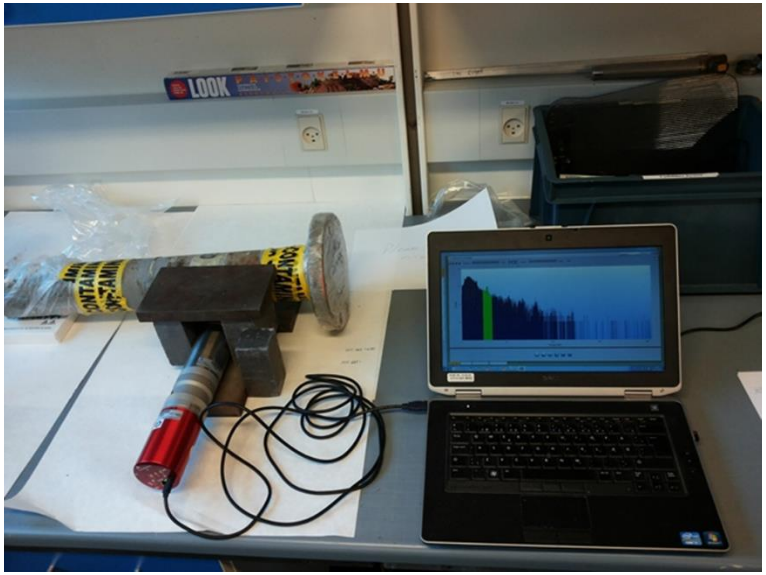
Scale (2.66g, 91 Bq/g Ra-226)) from tube nr 7. Note the Ac-228/Tl-208 lines (911 keV and 2614 keV)

Further on inhomogeneity
Direct readings using a NaI-detector (2”) on 609 keV

	NaI-cps 609 keV
Tube-7	25,34
	26,43
	23,42
	23,13
	21,62
	22,83
	23,45
	26,03
	27,08
	22,32
Average cps (609 keV)	**24,165**
1 Stdev	1,8941
%Stdev	7,8380



	NaI-cps 609 keV
Unlabelled tube with collar	2,35
	2,34
	1,98



Tube No 3 0,1-0,3 cps

Tube 1A < 0,1cps

Inhomogeneity tube No1

	cps	cps	cps	cps	cps	cps		cps	cps
	214Pb	**214Pb**	**214Bi**	**214Bi**	**214Bi**	**214Bi**		**228Ac**	**228Ac**
	0,193	0,376	0,461	0,151	0,058	0,154		0,113	0,158
	295 keV	**352 keV**	**609 keV**	**1120 keV**	**1238 keV**	**1765 keV**		**338 keV**	**968 keV**
POSITION-1	4,397	7,839	7,744	1,985	0,789	1,512		0,205	0,148
POSITION-2	4,108	7,471	7,159	1,913	0,711	1,477		0,244	0,084
POSITION-3	4,201	7,875	7,600	1,785	0,750	1,478		0,175	0,121
POSITION-4	3,940	7,194	7,451	1,840	0,736	1,469		0,173	0,098
POSITION-NED	3,781	6,764	7,048	1,704	0,628	1,348		0,259	0,072
POSITION-UPP	2,558	4,727	4,817	1,297	0,398	0,926		0,197	0,092
Average	**3,831**	**6,979**	**6,970**	**1,754**	**0,669**	**1,368**		**0,209**	**0,102**
1 stdev	0,66	1,18	1,09	0,24	0,14	0,22		0,04	0,03
% stdev	17	17	16	14	21	16		17	27

- Tube No1 shows a scale inhomogeneity of about 20% for the uncollided gamma in the present set-up.
- Dose rate variation will be less due to scattering.

Conclusions from direct gamma spectrometry of tubes

- Radioactivity content varied from about 100 to 10 Bq/g of ^{226}Ra in scale between the tubes received.
- Radioactivity distribution is spatially homogeneous with variations in the order of 10% or less on the decimetre scale.
- Intensity ratio 860 keV to 911 keV (^{208}Tl and ^{228}Ac) shows ^{228}Th/^{228}Ra less than 10%.
- ^{228}Ra/^{226}Ra ratio is about 10% (from ^{228}Ac 338 keV to ^{214}Bi 352 keV).
- Good news since ^{208}Tl results in a significant exposure through the 2614 keV line (100%).

Possible candidates for decay or build-up over a time period of days.

- Rn-222 escape
- Ra-226 – Rn-222 build-up (days-weeks)
- Ra-224 decay and buildup of daugters (days)
- Ra-223 decay and buildup of daugters (minutes)
- Loss of Rn-220 and decay of Pb-212/Bi-212/Tl-208. (minutes-hours)

Escape of radon from dry scale...?

- Contribution from radon-daughters to dose is more than 80% in these kind of scales.
- Any losses of radon thus make a major impact in the exposure rate.
- BaSO4 well documented for it's capacity to keep radon within it's lattice.

Intact scale (Tube-7) sealed for 1 month

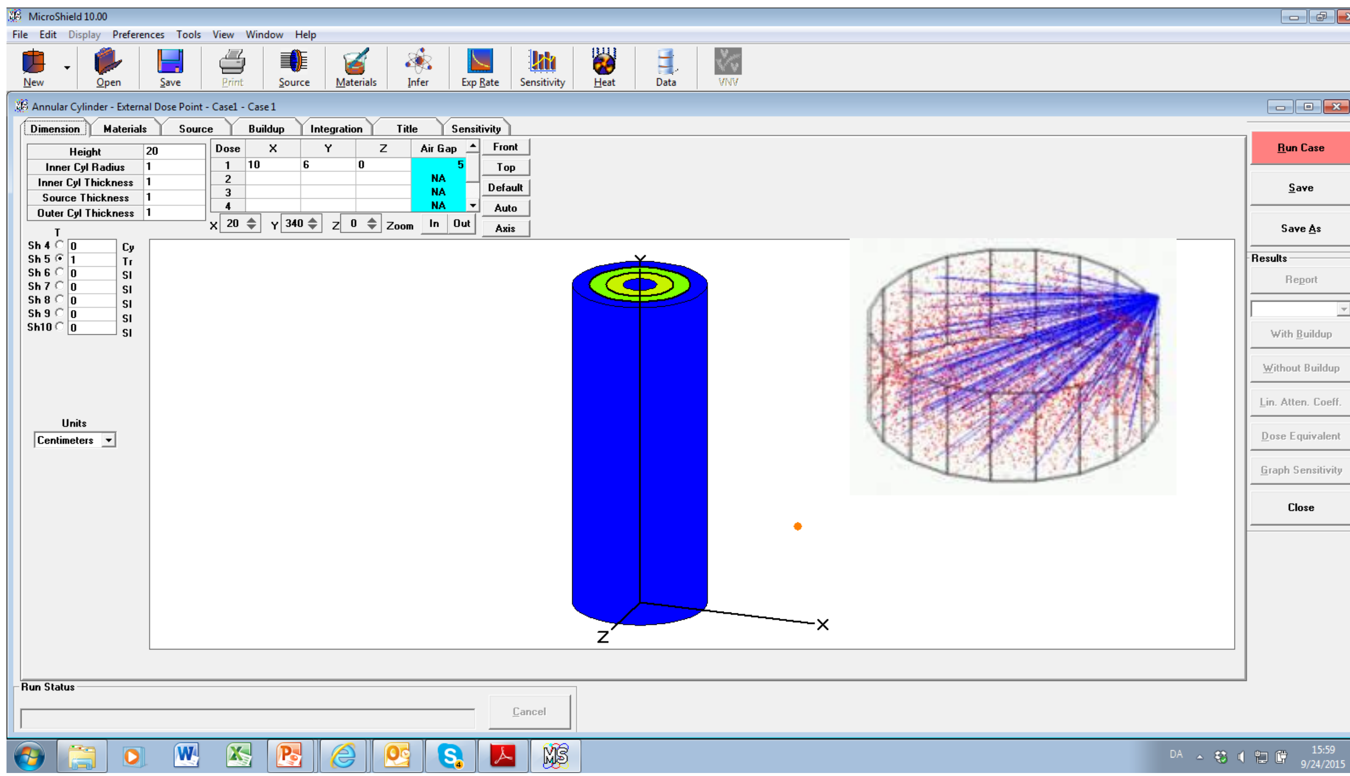
Analysed ^{222}Rn flux < 10% of decay.

Influence of selected parameters on external gamma dose-rate

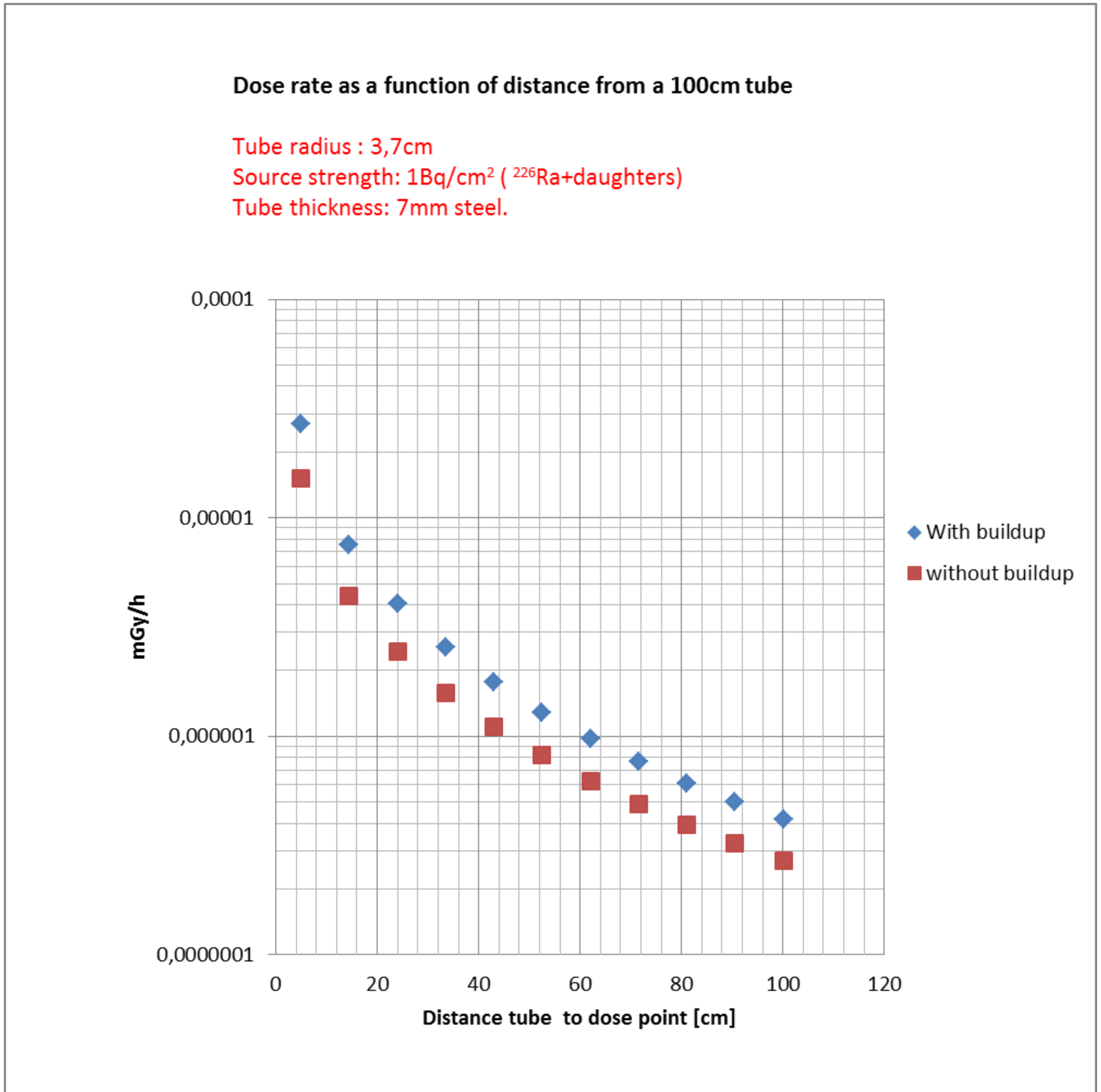
The important parameters governing the dose rate from a steel tube at a given source strength are:

- Tube length.
- Tube wall thickness.
- Distance from tube.
- Scale thickness, density, composition.

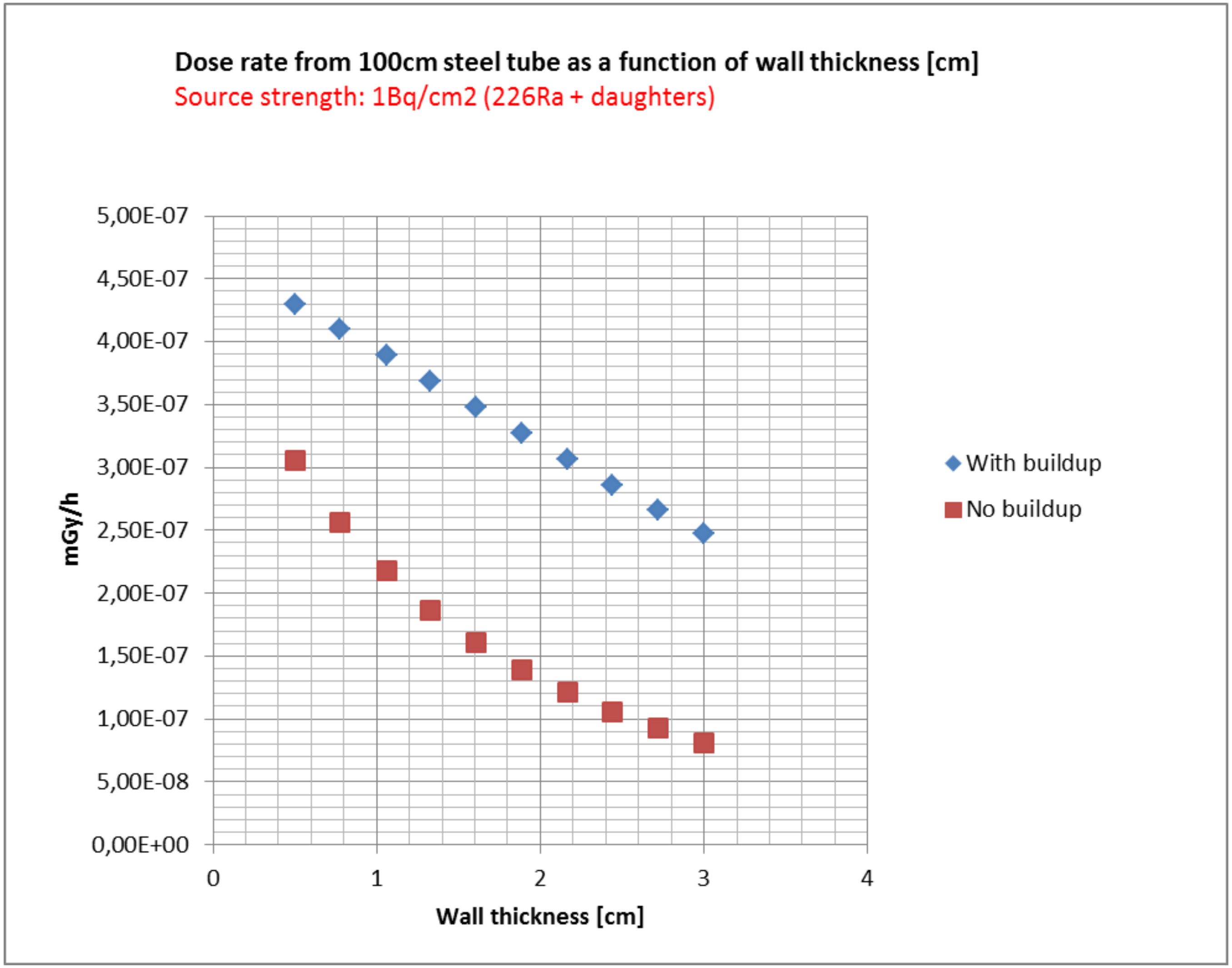
Calculations done using point-kernel method via Microshield.



Distance detector-tube

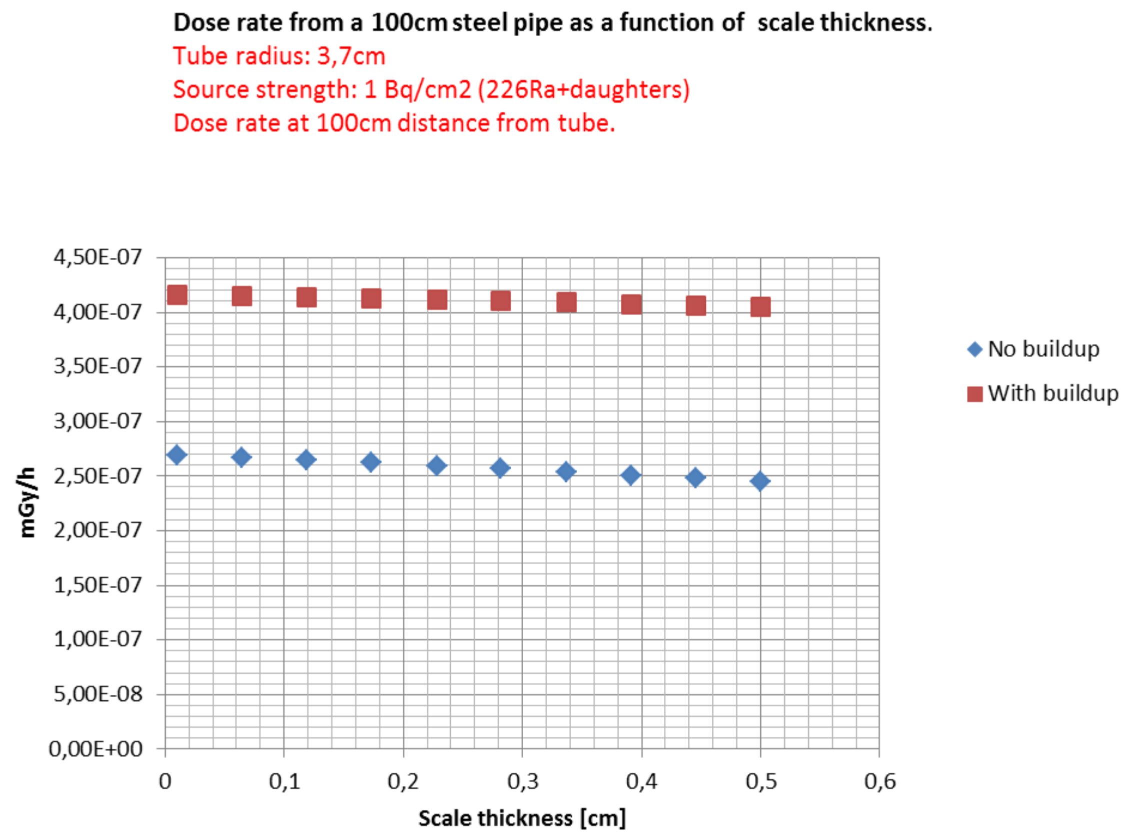


- The sensitivity to the distance becomes less the longer the tube is.



- The thickness of the steel wall has far more importance than the thickness or water content of the scale.
- Retention of radon daughters may be very different in wet vs dry scale

Scale thickness (constant activity)

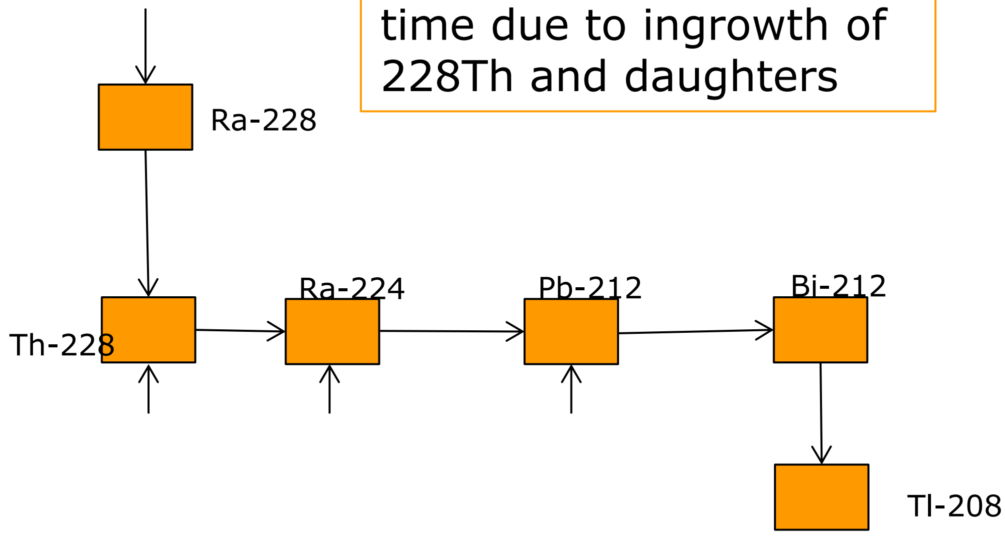


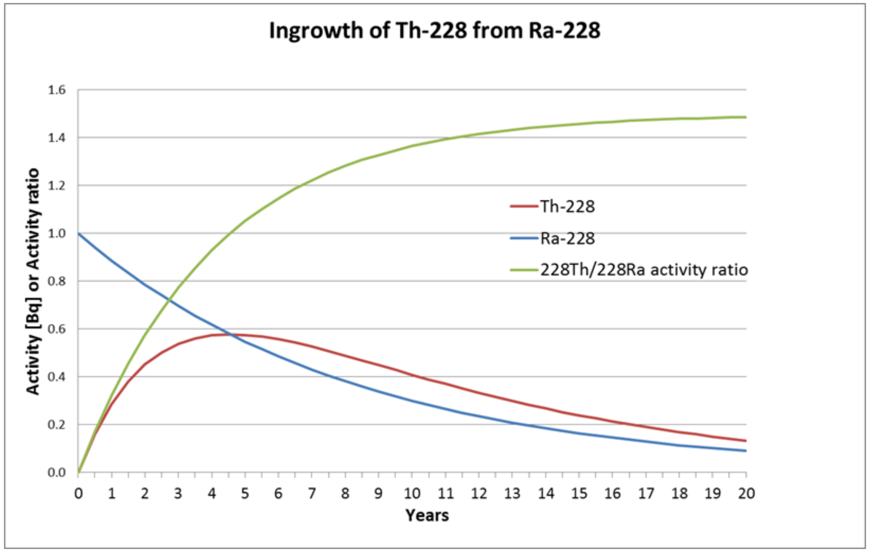
- Density of barite used is 3.35g/cm3. Compared to the steel shield this layer is of little importance.
- Various water content of the barite makes not much of a difference.

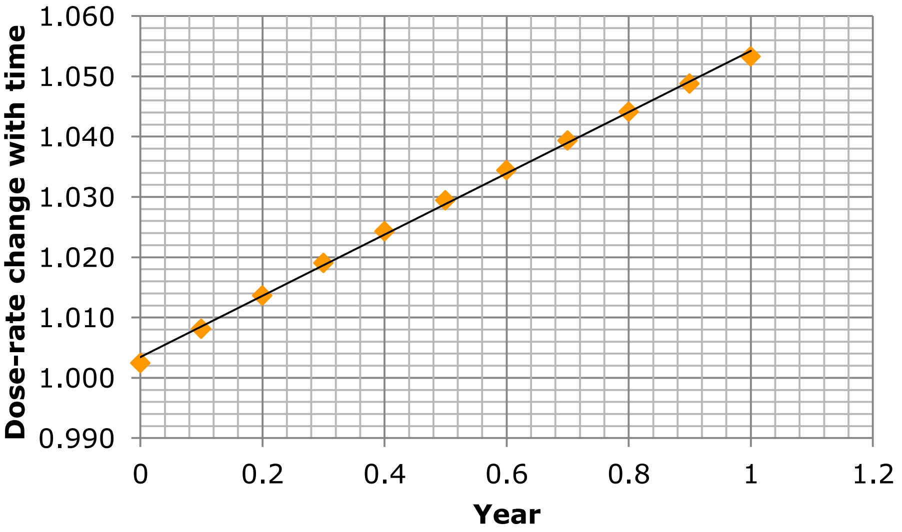
Possible explanations for different dose-rate readings

- Dose rate dependence on wet versus dry scale (self absorption) is insignificant for the 1-2mm scale deposits we have seen.
- Radon escape seems to be small (a few % for dry scale and less for wet scale) but varians is probably large.
- $^{228}Ra/^{226}Ra$ in fresh tubes is about 8%.
- $^{228}Th/^{228}Ra$ in fresh tubes is about 10%
- Both ratios above are functions on deployment time and time following uptake of tube.
- Short-lived ^{224}Ra & ^{223}Ra not in significant excess in the water phase (produced water). Not likely to play a role in time-dependent dose rate from scale.
- ^{210}Pb-^{210}Bi-^{210}Po ingrowth too slow to be of importance for the dose rate and gamma-emission is low.

Dose-rate change with time due to ingrowth of 228Th and daughters







CONCORE-Second part:

Review of existing methods to perform initial characterization of NORM contaminated equipment

Instructions on how to characterize or screen material containing NORM

13 guidelines (metrological instructions) examined:

- 4 from national authorities
- 7 from operators
- 2 written by international organizations

Instrumentation used:

- Dose rate meters (DRM).
- Contamination monitors (some with beta sensitive probe).
- Measuring with the "puck" method + contamination monitors.

Summary of reviewed guidelines

- Only 5 out of 13 guidelines specify that a fixed detector-object distance is important.
- 6 of the guidelines recommend doing measurement on wet material (avoid dust). Remaining guidelines do not adress wet vs dry measuerments.
- None of the thirteen guidelines address directly the challenges of measuring items with different geometry

Conclusion

- Variable equipment on-shore/off-shore, staff and procedures judged as the main reason for observed variability.