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IFE JOURNAL OF SCIENCE AND TECHNOLOGY

Vol 6. No. 1 (2022) 52–61

Possibilities of rapid assessment of norm in oil rig waste products for environmental compliance monitoring

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Abstract

Evaluation of Naturally-Occurring Radioactive Materials (NORMs) traditionally takes about a month to accomplish. This is because two of the major naturally-occurring primordial radioisotopes, ^{238}U and ^{232}Th, decay into daughter products, which are themselves serially radioactive. Included in both series is the radon gas, which continuously diffuses away, and therefore keeps the system in perpetual disequilibrium. The one-month wait is therefore required to seal up the sample after preparation and allow for the establishment of secular equilibrium within the series. This technical situation could have enormous socio-economic implications in applications, where NORMs need to be routinely evaluated as rapidly as possible. One major example is in the tons of waste products from the oil and gas industry, which could be deployed for other economically-beneficial applications in the public space, provided their compliance with relevant regulatory limits for radioactivity level could be ascertained in a timely manner. Previous workers trying to resolve this quagmire had suggested innovative protocols involving sequential counting of the sample on different days. However, these are generally too complex and laborious for routine applications, especially in an industrial setting involving many samples. In this work, we have directed our attention primarily on incinerated ash obtained as secondary waste from oil sludge, and clinkers produced with this ash. We simply evaluated the activity concentrations attributed to the ^{238}U and ^{232}Th series in the two matrices at various pre-secular equilibrium waiting periods, and compared with results obtained after secular equilibrium. By applying basic principles of risk assessment, we could then propose that samples with maximum activity level of 1,175Bq/kg for ^{238}U and 700 Bq/kg for ^{232}Th measured at any time pre-equilibrium, will meet the 10,000Bq/kg limits specified in the Nigeria Basic Ionizing Radiation Regulation 2003, for both radionuclides at secular equilibrium.

Keywords: Activity concentration; NORM; Secular equilibrium; Incinerated ash; Clinkers

Introduction

Tons of sludge are produced annually as waste products from oil rigs in Nigeria (Elegba and Funtua, 1999). It has been shown that these "wastes" could, in fact be used, not just as fuel in certain energy-intensive industries, they could also serve as input raw materials in the production of other important products such as clinker and asphalt (Gray 1993). However, the environmental impact of such applications needed to be carefully assessed ahead of deployment into public space, with appropriate mitigation measures provided as might be necessary.

Considerable amount of Technologically-Enhanced Naturally Occurring Radioactive Materials (TE-NORM) is associated with exploration and production activities in the oil and gas industry (Gray 1990, Elegba and Funtua 1999). Whereas chemical and biological toxicants within the sludge could be dealt with by various thermal and chemical procedures within standard waste treatment facilities, the radioactive materials within the wastes are hardly impacted, but might rather become more concentrated in the resulting incinerated ash produced by these procedures.

The geology of the oil formations, and their chemical conditions from time to time, affect such key parameters as concentrations, solubility, and diffusivity of radionuclides that accrue in the sludge and consequently in the incinerated ash (Gray 1993; Hussain-Subber, Ali and Al-Mosawy, 2014). Prior to further processing into end products for the general public therefore, each batch of ash (secondary waste) will need to be monitored for compliance with extant regulations stipulating allowed limits for TE-NORM. This requires protocols and infrastructure that would enable rapid and routine assessment.

Characterization of radioactivity requires that the various contributing radioisotopes be identified. This enables the sources of the radionuclides (whether anthropogenic or natural) to be ascertained. Thereafter, the levels of those NORMs are checked against the limits stipulated in the relevant regulations for each of the contributing radioisotopes (weighted according to their potentials to cause biological damage). Gamma spectrometry is the choice methodology for this exercise.

Virtually every radionuclide of concern has associated gamma radiation which can be rapidly detected and used to uniquely identify and quantify its activity-concentration in a given sample. This can be done with minimal sample preparation without any recourse to time-intensive chemical separations needed for other techniques.

Principally, on account of their very long (primordial) half-lives, the relevant naturally-occurring radionuclides are ^{40}K (half-life 1.25 x 10^{9} yr), ^{238}U (half-life 4.5 x 10^{8} yr), and ^{232}Th (half-life 1.41 x 10^{10} yr). ^{40}K decays by both electron capture (EC)/positron decay (10.72%) and β^{-}decay (89.28%). The gamma radiation of energy 1460 keV is associated with the EC/positron emission to ^{40}Ar. ^{40}K can therefore be easily determined immediately after sample collection using this gamma energy. However, ^{238}U and ^{232}Th decay into daughter products which are themselves serially radioactive, until they eventually form ^{206}Pb and ^{208}Pb, respectively. As the activity of a radionuclide at any given time depends on the amount of it that is present (exponential decay), the activity of each radionuclide in a series self-adjusts continually, until all of them come to the same final activity after a sufficiently long period. This is known as secular equilibrium and the process is described mathematically by the Bateman equations (Bateman, 1910). With the attainment of secular equilibrium, any of the radionuclides that is convenient to measure can then be used to determine the activity of the series. However, both the ^{238}U and ^{232}Th series include radon gas as family members, viz ^{220}Rn in the ^{232}Th series, and ^{222}Rn in the ^{238}U series. The inevitable continuous leakage of this gas continuously hinders the attainment of secular equilibrium. This, therefore, necessitates that a given sample to be evaluated for ^{238}U and ^{232}Th should first be sealed up to prevent escape of radon and allow the subsequent attainment of secular equilibrium. Assuming no previous stored-up radon in the sample, the time required for the attainment of secular equilibrium in both the ^{238}U and ^{232}Th series is generally taken to be about 28 days (Wei *et al* 2015, Alvarez 2016, Ojo 2016).

The implication of this is that precise evaluation of ^{238}U and ^{232}Th would require a minimum of 28 days to be accomplished. This is a big draw back with dire implications for the sustainability of the whole concept of turning primary wastes in the oil and gas sector into useful by-products for the benefit of the public. Several efforts have been made, and are being made, to circumvent this time-consuming default protocol. The general concept revolves around making efforts to predict the equilibrium value of a suitable member of the series through measurements taken long before the equilibrium is reached. This is generally accomplished at the expense of accuracy in the result, and is reflected as larger uncertainty/error values. For regulatory compliance monitoring purposes however, this larger value of uncertainties might be inconsequential.

For a simple anthropogenic serial radioactivity with well-characterized initial conditions, the Bateman equation could be used directly to predict the final equilibrium values as demonstrated by Cong Wei et al (2019) for the ^{90}Sr/^{90}Y system. For NORMs however, the initial conditions are not so well defined, and the equation becomes quite complex to handle. It is usually considered expedient to introduce approximations for handling particular radioactive series; and sometimes for specific matrices under certain well-defined constraints. For instance, Li *et al* (2015) described the "^{214}Pb ingrowth method" which permits a "rapid and sufficiently accurate" determination of ^{226}Ra activity without the need to wait for ^{226}Ra – ^{222}Rn equilibrium. However, it requires the sequential counting of ^{214}Pb on three different days, which could be both complex and laborious for routine applications, especially where several samples are involved, and limited number of detectors are available. Wilson *et al* (2019) tried to improve on the accuracy of the results by including the simultaneous measurement of the activity of ^{214}Bi together with that of ^{214}Pb. They also needed to introduce a number of assumptions to simplify their computer simulation, *viz*: the sample is at least 6 million years old, and had attained secular equilibrium with all of its progeny prior to the sample collection and preparation during which only 33% of the ^{222}Rn escaped, enabling a rapid re-establishment of secular equilibrium upon subsequent sealing of the sample. Van Cleef (1994) had been able to obtain similar results with a much simpler method by restricting his analyses only to minimally processed soil samples, where the ^{222}Rn gas may be assumed to have remained trapped within the crystal lattice structure such that the sample is practically at secular equilibrium right from the field.

In this study, we have focused specifically on incinerated ash obtained as secondary waste from oil sludge, and clinkers produced (end product) from the ash for use in the cement industry. We simply compare the results obtained from early pre-equilibrium analyses, and those obtained post-equilibrium to ascertain whether or not there are clear relationships that could facilitate rapid determination of the compliance status of a given sample (of these two types), with the regulatory limits, based on measurements made long before the 28 days stipulated for attainment of secular equilibrium.

Materials and Methods

Collection of Materials

The materials comprised of incinerated ash samples (secondary waste) and clinker samples as end products obtained from the ash. Ash was evacuated from the primary waste treatment plant for oil rig sludge within the facility of an oil and gas operator in Lagos. Samples of the incinerated ash were analysed for NORM batch-by-batch, after which they were used as input to produce clinker in a cement plant. This process involved subjecting the ash to high material temperature (typically 1450°C) at a residence time of about 30 minutes within the rotary kiln. Radioactivity levels were thereafter assessed also in the clinker samples for comparison with their levels in the corresponding batch of incinerated ash. In order to clarify the preliminary results obtained, a soil sample from the Niger delta was also further analysed.

Sample Preparation and Gamma Spectrometry

Clinker samples were crushed, pulverized, and homogenized using a commercial pulverizer. Two hundred milligram aliquots of each sample were weighed out and sealed with cellotape in our regular counting polyethylene (PE) bottles. Olive oil was applied to the cellotape to improve the seal. Samples of ash, being in powdered form already, were simply homogenized before they too were dispensed, 200 mg each into the PE bottles and sealed up. Each of the samples was counted for periods ranging from 8 to 10 hours at the same standard geometry using our extensively-shielded gamma spectrometer facility, employing a 1” x 1” CsI detector.

The specific activity for ^{238}U was calculated from the spectrum obtained for each sample as the area of a specified Region of Interest (ROI) around the 609.3 keV peak of ^{214}Bi, compared with the peak area under the same ROI obtained from the IAEA S-385 SOIL and ENV94084 (Rocketdyne Environmental Lab) reference materials. The result with the better counting statistics (less uncertainties values) from these two reference materials is chosen. The peak area for ^{228}Ac (at 911.2 keV) was used in a similar manner for the determination of ^{232}Th in each sample. These computations were facilitated by a programmed Spreadsheet developed in our laboratory.

The error in the individual measurement is taken as error in the counting statistics ($\sqrt{N}/N$) according to Poisson distribution, N being the number of counts); and error in the setting and use of fixed ROIs for different samples when there indeed might be electronic drift rendering the ROI not necessarily optimal for all the samples. This uncertainty was estimated by comparing the actual range (as returned in the Peak Reports for each sample by the MCA software) with that used for the standard in the comparator evaluation; and translating this to uncertainty in calculated peak areas ΔA (i.e. $\Delta A = 2\Delta R$, where ΔR is the uncertainty associated with the ROI). The uncertainties derived in this way were found to be compatible with what was needed to keep the activity concentration of ^{40}K constant irrespective of the "waiting periods", as expected, given its 1.25 billion years half-life.

Results and Discussion

The activity-concentration for the ^{238}U series using ^{214}Bi and that for ^{232}Th using ^{228}Ac, various days after sealing of the vials before secular equilibrium; and similarly-determined activity-concentration after secular equilibrium, are shown in Table 1 for incinerated ash and in Table 2 for clinker. There is no clear pattern in the relationship between the activity levels in ash and clinker. While the heating process in the rotatory kiln might result in the release of some volatile forms of radionuclides, and other additives might further lead to some dilution, the dehydration on the other hand might serve to further concentrate the radionuclides. The difference in densities will not matter, since the clinker is first pulverized before measurement, and the activity concentration is subsequently normalized by the mass of the aliquot measured.

For ^{238}U in incinerated ash, pre-secular equilibrium levels were greater than post-secular equilibrium values for all the samples except two, Y5 and Y6. But the differences in the mean and variance of the two sets were not statistically significant. Significantly for our interest, the highest variation observed for ^{238}U in incinerated ash was 25% (in sample Y6).

Similarly for ^{232}Th, there was neither a clear pattern nor a statistically significant difference in the mean values for pre- and post-secular equilibrium. However, the highest increase between pre- and post-equilibrium values was 94% in Sample Y1. It might be noted, however, that there was an even higher difference in the other direction (a decrease) between pre- and post-equilibrium values. This was 133% recorded for sample Y3.

In the corresponding clinker samples (Table 2), ^{238}U levels follow the same trend as in incinerated ash in which the pre-secular equilibrium values are generally higher than post-secular equilibrium values (except for two samples, T1 and T3). However, the mean of the two sets were not statistically significant. The highest increase between pre- and post-equilibrium values was 57% in sample T3. But the highest variation (a decrease) in the two sets was 75% in sample T7.

The situation for ^{232}Th in the clinker was similar to that in incinerated ash.It should be noted in these discussions, that the "pre-secular equilibrium" counting started after Day 14 through Day 19. It is possible that the samples were already near equilibrium by this time, depending on the thermal and other processing history from the field to the laboratory. In order to investigate what the picture might look like in the earlier days, we counted a soil sample from the Niger delta, on various days after sealing, from Day 0 to Day 28. The result is presented in Table 3. There was no clear trend both for ^{238}U and ^{232}Th. However, there was a somewhat significant decrease **($p < 0.0581$)** in ^{232}Th level between Day 0 (41.9 ± 7.4) Bq/kg and Day 28 (19.9 ± 2.6) Bq/kg - a 116% decrease.

Table 1: Pre-Equilibrium (14 – 19 days after sealing) and Post-Equilibrium (≥28 days after sealing) [Incinerated Ash]

Sample ID	**^{238}U**			**^{232}Th**	
	Days after Sealing	Pre-Secular Equilibrium Activity (Bq/kg)	Post-Secular Equilibrium Activity (Bq/kg)	Pre-Secular Equilibrium Activity (Bq/kg)	Post-Secular Equilibrium Activity (Bq/kg)
Y1	14.0	17 ± 1	13 ± 1	16 ± 3	31 ± 5
Y2	14.5	40 ± 3	36 ± 3	47 ± 8	54 ± 8
Y3	15.8	39 ± 3	33 ± 3	63±11	27 ± 4
Y4	15.5	36 ± 3	30 ± 3	53 ± 9	48 ± 7
Y5	15.0	27 ± 2	31 ± 3	46 ± 8	34 ± 5
Y6	16.0	40 ± 3	50 ± 5	77 ± 14	55 ± 8
Y7	16.5	60 ± 5	56 ± 5	72 ± 13	58 ± 8
Y8	17.0	41 ± 3	41 ± 4	55 ± 10	43 ± 6
Y9	18.5	42 ± 3	31 ± 3	62 ± 11	50 ± 7
Y10	18.0	53 ± 4	49 ± 5	73 ± 13	81 ± 12
Mean ± SD	**16.1 ± 1.5**	**39.5 ±12.0**	**37.0 ± 12.0**	**56.4 ± 16.9**	**48.1 ±14.9**

Table 2: Pre-Equilibrium (7 – 11 days after sealing) and Post-Equilibrium (≥28 days after sealing) [Clinker]

Sample ID	**^{238}U**			**^{232}Th**	
	Days after Sealing	**Pre-Secular Equilibrium Activity** (Bq/kg)	**Post-Secular Equilibrium Activity** (Bq/kg)	**Pre-Secular Equilibrium Activity** (Bq/kg)	**Post-Secular Equilibrium Activity*** (Bq/kg)
T1	7.0	27 ± 2	40 ± 6	29 ± 4	44 ± 14
T2	8.0	47 ± 3	29 ± 4	45 ± 6	41 ± 12
T3	8.5	30 ± 2	47 ± 7	52 ± 7	34 ± 11
T4	8.8	41 ± 3	39 ± 6	55 ± 7	48 ± 15

T5	9.0	43 ± 3	35 ± 5	53 ± 7	61 ± 19
T6	9.5	46 ± 3	41 ± 6	46 ± 6	38 ± 12
T7	9.8	49 ± 3	28 ± 4	55 ± 7	47 ± 15
T8	10.0	44 ± 3	42 ± 6	45 ± 6	50 ± 16
T9	10.5	43 ± 3	36 ± 5	46 ± 6	55 ± 17
T10	11.0	46 ± 3	40 ± 6	60 ± 8	51 ±16
Mean ± SD	**9.2 ± 1.2**	**41.6 ± 7.3**	**37.8 ± 5.7**	**48.6 ± 8.6**	**46.8 ± 8.4**

* These samples were counted only for 1 hour each, and therefore have a larger associated uncertainties.

Table 3: Activity for ^{238}U and ^{232}Th for the Same Soil Sample (from the Niger Delta) After Various Pre-Equilibrium Sealing Times

Days after Sealing	**^{238}U (Bq/kg)**	**^{232}Th (Bq/kg)**
0	14.4 ±1.9	41.9 ± 7.4
11	16.0 ±1.5	25.6 ± 3.7
12	16.06±1.6	25.1 ± 3.6
13	15.2 ± 1.5	27.2 ± 3.9
14	15.2± 1.5	26.2 ± 3.8
15	14.0± 1.4	25.1 ± 3.6
16	16.2 ±1.6	22.5 ± 3.3
17	17.5 ± 1.7	20.9 ± 3.0
18	17.1 ± 1.7	23.6 ± 3.4
19	15.5 ± 1.5	29.8 ± 4.3
20	14.5± 1.2	30.9 ± 4.0
21	16.3 ± 1.3	31.4 ± 4.1
24	17.1 ± 1.4	28.3 ± 3.7
25	15.6 ± 1.3	26.1 ± 3.4
28	15.1 ± 1.2	19.9 ± 2.3

The variation in radioactivity for a radioactive series on its way to attaining secular equilibrium, just as the Bateman's equation modeled it, is quite complex. The actual solution at a particular day is strongly dependent on the boundary conditions, in particular the initial level of the radon locked up in the crystals. Hence it depends on the history of the sample: from the field, subsequent processing (e.g. during conversion to ash/clinker) and finally, before the processing at the spectrometry laboratory and sealing. In other words, the journey towards attainment of secular equilibrium does not begin with the sealing done in the laboratory.

As pointed out earlier, Wilson *et al* (2019) assumed that only 33% of radon had escaped from the sample matrix before getting to the laboratory, while Van Cleef (1994) assumed

100% secular equilibrium from the start for some soil samples if sample processing is reduced to the barest minimum. This condition, however, implicitly means not having the sample and reference standard in the same physical form (highly homogenized powder, liquid, or gel), which is required to improve the accuracy of the comparator method by ensuring similar level of internal self-shielding.

The results presented here, obtained from measurements carried out in our laboratory support the notion that most of the incinerated ash and clinker samples were not far from secular equilibrium for the two series right from their arrival in the laboratory. For the ^{238}U series, the maximum change in activity for incinerated ash was 25% (in Sample Y6) and that in Clinker was 75% (Sample T7). For ^{232}Th, the maximum variation was -133% (Sample Y3). In the Soil sample, the maximum variation for ^{232}Th was 116%.

For our purpose, it is therefore possible to suggest maximum values for ^{238}U and ^{232}Th expected for a sample counted immediately on arrival at the laboratory and check if this will fall within the stipulated regulatory limits. Borrowing from basic principles employed in Environmental-Health Risk Assessment, values depicting worse-case scenarios (Point of Departure values, e.g. “No Observable Adverse Effects Levels”) are experimentally derived, and these are subsequently modified by some “uncertainty factors” to take care of discrepancies that might arise in other experimental conditions elsewhere. To account for uncertainties in the “quantity and quality” of the scientific data, (which is the only factor applicable in this case) a factor of 10 is traditionally used [WHO 1990, EnHealth 2012]. Therefore, we hereby propose that the maximum variations observed in this work, between activity levels before and after secular equilibrium, be further multiplied by a factor of 10; and that this be taken as the maximum variation that could arise in a clinker or incinerated ash sample counted anytime without consideration for the secular equilibrium status.

For ^{238}U, the maximum variation between pre-equilibrium and post-equilibrium values was 75% recorded for sample T7 (clinker), while the corresponding value for ^{232}Th was 133% recorded for sample Y3 (incinerated ash). By our proposition, these variations, in some other experimental setups could rise to a maximum of 750% for ^{238}U and 1,333% for ^{232}Th. Thus, if the pre-equilibrium activity level for ^{238}U in clinker or incinerated ash is X, the maximum increase that could be reasonably expected post-equilibrium would be 7.5X; while a maximum post-equilibrium value of 13.3Y would be reasonably expected for ^{232}Th in a clinker or incinerated ash sample where Y is the value obtained anytime pre-equilibrium. These values can then be checked against the regulatory limits thus permitting rapid evaluation of these particular samples for the very important applications identified in this paper.

Specifically, samples with maximum activity level of 1,175Bq/kg for ^{238}U and 700 Bq/kg for ^{232}Th measured at any time pre-equilibrium, will meet the 10,000Bq/kg limits specified by the Nigerian Nuclear Regulatory Agency (NNRA) in the Nigeria Basic Ionizing Radiation Regulations 2003, for both radionuclides at secular equilibrium [NNRA 2003; 8th Schedule, Column 2, page B229].

Environmental and Safety issues in the Oil and Gas industry is managed by the Department of Petroleum Resources, DPR (now called the Nigerian Upstream Petroleum Regulatory Commission - NUPRC), and the radioactivity levels allowed in the industry are specified in the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN), first issued by the DPR in 1991 and revised in 2018 (3rd edition). EGASPIN screening limits for ^{238}U and ^{232}Th at 1,000 Bq/kg are an order of magnitude more stringent than the general regulation by the NNRA. (DPR 2018; Part III, Section 5.3.6.4.2.2, page 35), and by our recommendation in this paper, pre-equilibrium activity levels meeting these limits would be 118 Bq/kg and 70 Bq/kg for ^{238}U and ^{232}Th respectively.

An interesting question to ponder is whether or not the EGASPIN limits should be applicable in the case under consideration here. Though the waste is generated in the oil and gas sector, the ultimate application is in the cement industry, which is not under the purview of the DPR/NUPRC.

Conclusion

We have demonstrated that the uncertainties in the levels of radioactivity measured for the serially -radioactive nuclides ^{238}U and ^{232}Th in clinker and incinerated ash may not justify the traditional month-long waiting for attainment of secular equilibrium before they are evaluated. If the activity level measured at any time is less than 1,175Bq/kg for ^{238}U and 700 Bq/kg for ^{232}Th, then applying the standard practice used in environmental health risk assessment, the activities in the samples may be reasonably presumed to be compliant with the extant regulatory limits of 10,000 Bq/kg at secular equilibrium. The socio-economic implications of this position could be huge with respect to the sustainable development in our country.

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