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Disequilibrium in the uranium and actinium series in oil scale samples

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ABSTRACT

We have investigated the disequilibrium of the uranium and actinium series and have found both ^{226}Ra (90,200 ± 4300 Bq/kg) and ^{228}Ra have activity concentrations orders of magnitude higher that ^{238}U (1.83 ± 0.36 Bq/kg) and ^{232}Th (7.0 ± 0.4) which are at the head of the decay series. As well the activity concentration of ^{210}Pb (24,400 ± 1200 Bg/kg) was about 3.6 times less than ^{226}Ra. Once an efficiency curve was constructed summing corrections for specific isotopes in the decay change also needed to be taken in consideration. Furthermore, self-attenuation of the photons especially the 46.5 keV belonging to ^{210}Pb was calculated to be 78% since the scale had elevated elemental concentrations of high-Z elements such as barium and strontium.

1. Introduction

Radiation in the oil exploration industry was identified very early in the 20th century (McLennan, 1904), a short eight years after Becquerel discovered radioactivity. In the 1980's^{226}Ra began to be noticed when scrap metal dealers would detect unacceptably high levels of radiation from oil-field piping (Zielinski and Otton, 1999). Technically enhanced naturally occurring radioactive material (NORM), also known as TENORM, will develop in high activity concentrations in by-product oil and gas waste streams (Al-Saleh and Al-Harshan, 2008; Gazineu and Hazin, 2008). The TENORM will chemically separate from other piped material in the process of the extraction of oil, resulting in high activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb and other radioisotopes in a densely caked layer on the inner surfaces of the piping, which is called scale. Sludge is often part of the process and is also elevated in activity concentrations. The activities in scale of the ^{226}Ra, ^{228}Ra and ^{210}Pb can range from 100–1.5 × 10^7 Bq/kg, 50–2.8 × 10^6 Bq/kg and 20–7.5 × 10^4 Bq/kg, respectively. (IAEA, 2003). The environmental pathways of uranium and thorium and their daughter products are different in the oil fields and as such disequilibrium can occur. There have been a multitude of studies involving the disequilibrium of mainly uranium and to a lesser degree actinium series in environmental samples. Some investigations include reference materials (Colaianni et al., 2011), fractionation of natural radionuclides in soils from the vicinity of a former uranium mine (Štrok and Šmodis, 2010) and uranium isotopes in bottled mineral waters (Gharbi et al., 2010). To this date there appears to be no systematic analysis of the possible disequilibrium in either the uranium or actinium series in oil scale. Since there are unusually high activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb oil scale, we decided to investigate if disequilibrium exists.

2. Experimental

2.1. Sample preparation

A large batch of scale sample from west Texas was provided by Enviroklean Product Development Inc. (EPDI) which was first dried in an oven for 24 h at 105 °C. About 100 g from the 1 kg batch was then sifted through 250 μm sieve in a large plastic bag to prevent any external contamination. Three 20.0 g samples were placed in a Petrie® dish (6 cm diameter by 1.5 cm height) and heat-sealed. Careful consideration was given to make sure that the Petrie® dish was filled as close to top to minimize any head space. To test the homogeneity of the three samples the net counts of gamma-rays of 46.1 keV (^{210}Pb), 186.4 keV (^{226}Ra) and 911.4 keV ^{228}Ac were compared and found that only a ± 3% variation existed for these photopeaks. This gave confidence in using this scale sample was representative of the original batch. The sample can be considered to be representative of those found in west Texas and not necessarily of scale samples in general.

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2.2. Calibration and radioactivity counting

For the calibration an eight point standard efficiency curve was constructed with a mixture of isotopes from Eckert and Zeigler Analytics from 46.5 to 1332.4 keV in water placed in a Petrie © dish as shown in Fig. 1. The isotopes used were ^{210}Pb (46.5 keV), ^{241}Am (59.5 keV), ^{109}Cd (88.0 keV), ^{57}Co (122.1 keV), ^{139}Ce (165.9 keV), ^{137}Cs (661.7 keV), and ^{60}Co (1173.2 keV and 1332.4 keV). The uncertainties on the activities ranged from 2.5% to 4.9% with an average of 3.69%. One 20.0 g sample of scale was counted for 12 h on an Ortec N-type Gamma-X detector with an efficiency of 33% and FWHM of 2.0 for the 1332 keV ^{60}Co photopeak. The use of a beryllium window instead of the usual aluminum one yielded a much better counting efficiency for the determination of the 46.5 keV gamma-ray belonging to ^{210}Pb. A typical gamma-ray spectrum is seen in Fig. 2. The analytical uncertainties based on counting statistics for all the radionuclides were all less than 1% except one at 7.6% with an average of 1.3%. The overall analytical and systematic uncertainties include those in the counting statistics in efficiency curve and in the samples, the certified calibration values, and the self-attenuation values (<1%), which have all been propagated. Summing corrections for a Petrie dish were taken from previously published work (Garcia-Talavera et al., 2001).

A quality control on the efficiency curve was performed by analyzing the IAEA-375 radionuclides in soil (IAEA, 2000) for ^{137}Cs. Our result of 5020 ± 160 Bq/kg was in good agreement with the consensus value of 5280 ± 80 Bq/kg, which is ~5% higher.

2.3. Interferences

There are two additional interferences that were taken into consideration. One is the interference of the 185.2 keV gamma-ray of ^{235}U on the 186.2 keV of ^{226}Ra. This interference is well known and explained (Gilmore, 2008). However, in these NORM samples the activity of ^{235}U is several orders of magnitude less than that of ^{226}Ra, thus having a negligible interference effect. The second systematic problem is coincidence summing. Again this is a recognized effect and for naturally occurring radioactivity these corrections have been tabulated for Marinelli and Petri® holders (Garcia-Talavera et al., 2001). For ^{210}Pb and ^{226}Ra the correction factors are negligible but the 911.2 keV photon for ^{228}Ac used to determine ^{228}Ra, there was a 9% effect. The results in Table 1 reflect this correction factor. Summing corrections for ^{214}Pb and its 351.9 keV photopeak and for ^{214}Pb and its 238.6 keV photopeak were zero and 2.5%, respectively for the results shown in Table 2.

2.4. Determination of uranium and thorium by neutron activation analysis

To elucidate the presence of equilibrium or disequilibrium the uranium or actinium decay series both ^{238}U and ^{232}Th need to determined. For ^{238}U there are two classic ways of determining its activity by gamma-ray spectroscopy. One way is using either of its daughter products of ^{226}Ra such as ^{214} Pb photopeak at 295.2 keV or the Bi photopeak at 609.3 keV after 30 days when secular equilibrium with ^{222}Rn is reached. Both these gamma rays have high emission probabilities thus yielding strong photopeaks. The second method is to use 1001.0 keV gamma-ray of ^{234m}Pa which is the first granddaughter of ^{238}U. However, this gamma-ray has a low emission probability and can only be effectively used with higher activity concentrations of uranium than typically found in environmental samples (Kapsimalis et al., 2009). For thorium there are also several options. One is gamma counting of ^{212}Pb with its 238.6 photopeak, ^{208}Tl with its two photopeaks of 583.2 keV, 2614.5 or ^{228}Ac with its two photopeaks of 911.2 or 969.0 keV. However, both methodologies are not feasible for either ^{238}U or ^{232}Th for disequilibrium investigations. In the case of ^{238}U if disequilibrium is suspected then ^{226}Ra or any of its decay products cannot be used. The direct counting of 1001.0 keV gamma-ray of ^{234m}Pa is not possible especially with the very high background in the scale (see Fig 2.) The case for ^{232}Th is similar. One cannot use ^{228}Ac to determine ^{232}Th if disequilibrium is doubted with its daughter ^{228}Ra and subsequent daughter products.

A unique way to overcome this dilemma is to use neutron

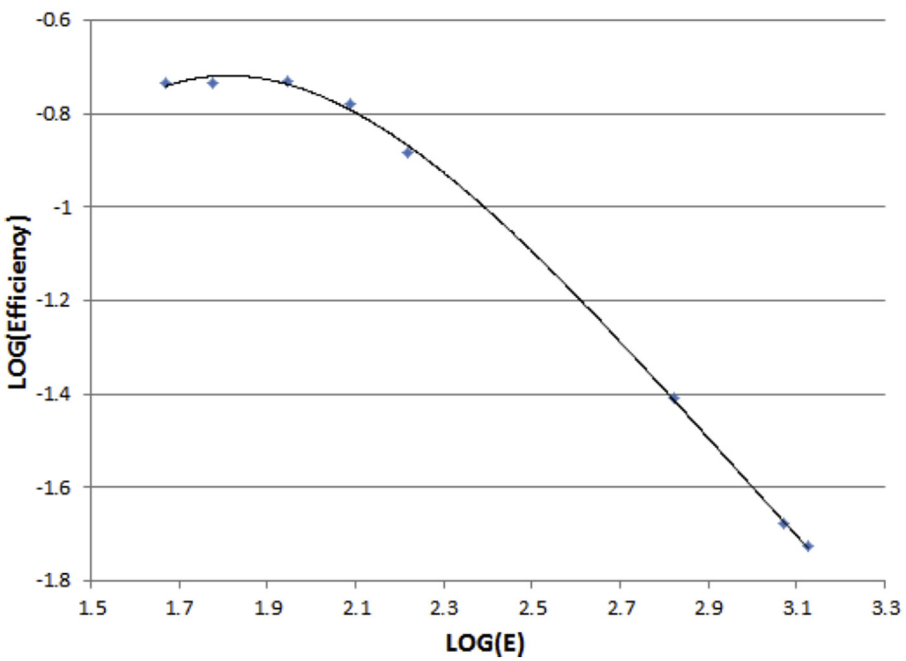

Fig. 1. Efficiency curve of a mixture of isotopes in water.

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