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Chemical composition of scales generated from oil industry and correlation to radionuclide contents and gamma-ray measurements of ^{210}Pb☆

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A B S T R A C T

Scale generated from the maintenance of equipment contaminated by naturally occurring radioactive materials may contain also chemical components that cause hazardous pollution to human health and the environment. This study spotlights the characterisation of chemical pollutants in scales in relation to *home-made comparison* samples as no reference material for such waste exists. Analysis by energy dispersive x-ray fluorescence, with accuracy and precision better than 90%, revealed that barium was the most abundant element in scale samples, ranging from 1.4 to 38.2%. The concentrations of the toxic elements such as lead and chromium were as high as 2.5 and 1.2% respectively. Statistically, high correlation was observed between the concentration of Ba and Sr, sample density, radionuclide contents (^{210}Pb and ^{226}Ra) and self-attenuation factor used for the radio-measurements. However, iron showed a reverse correlation. Interpretation of data with regards to the mineralogical components indicated that ^{226}Ra and ^{210}Pb co-precipitated with the insoluble salt $Ba_{0.75}Sr_{0.25}SO_4$. Since both Ba and Sr have high Z, samples of high density (ρ) were accompanied with high values of self-attenuation correction factors (C_f) for the emitted radiation; correlation matrix of Pearson reached 0.935 between ρ and C_f. An attempt to eliminate the effect of the elemental composition and improve gamma measurements of ^{210}Pb activity concentration in scale samples was made, which showed no correction for self-attenuation was needed when sample densities were in the range 1.0–1.4 g cm^{-3}. For denser samples, a mathematical model was developed. Accurate determinations of radionuclide and chemical contents of scale would facilitate future Environmental Impact Assessment for the petroleum industry.

1. Introduction

Naturally occurring radioactive materials (NORM) are widely recognised as a problem in countries with developing oil and gas industries. A significant contamination by radionuclides from ^{232}Th and ^{238}U series, which are present in varying concentration in hydrocarbon reservoirs, arises from their accumulation and co-precipitation with barium and strontium salts, forming a dense caked layer (ranging from μm to a few mm in depth) on the inner surfaces of processing equipment, separator vessels, wellheads, tubular and pipelines (Al-Saleh and Al-Harshan, 2008; Gazineu and Hazin, 2008; Heaton and Lambley, 1995). Descaling operations give rise to scale wastes. The activity concentrations of scales vary between several becquerels to thousands Bq/g of sample (Al Attar et al., 2015a; EPA, 2001; Godoy and Cruz, 2003; Zielinski and Otton, 1999). In addition to NORM, scales contain corrosion products, oil and heavy metals that would be more abundant than the radionuclides (i.e. mainly Ba and Sr as sulphates) (Gazineu et al., 2005; O'Brien et al., 2011; Varskog and Gellermann, 2011). NORM of low activity concentrations can be discharged to the environment, however, those of high concentrations are often classified as low level radioactive waste (IAEA, 2004; Liland et al., 2012; Read et al., 2004; Varskog and Gellermann, 2011; Zielinski and Otton, 1999).

Appropriate handling and disposal of scale waste require adequate chemical and radiochemical characterisation, which is a challenging task owing to their radioactivity content which greatly exceeds the environmental level, complex chemical composition and high density (Al Attar et al., 2015a; Gazineu and

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Hazin, 2008; EPA, 2001; Obiajunwa et al., 2002). Determination of the activity concentration in scale samples by gamma spectrometry is susceptible to sample-absorption, so-called self-attenuation due to the presence of heavy metals (with high Z), especially for low γ-energy lines (i.e. <100 keV); this effect can be corrected experimentally or theoretically (Al Attar et al., 2014; El Afifi and Awwad, 2005; Gazineu and Hazin, 2008; Habib et al., 2010, 2014; Hrichi et al., 2013). However, under- or over-estimation of the activity concentration of radionuclides cannot be ruled out.

Literature surveys show that limited studies have focused on estimating the chemical composition of oil-produced scale by energy dispersive x-ray fluorescence (EDXRF) (Al-Saleh and Al-Harshan, 2008; Al-Masri and Aba, 2005; El Afifi and Awwad, 2005; Hamlat et al., 2001; Obiajunwa et al., 2002). Although no or inappropriate reference materials have been used for elemental analysis, correlation to self-attenuation correction factors has not been considered.

As part of an on-going research programme to treat and manage oil solid wastes from the Syrian oil fields, a primary study (Al Attar et al., 2015a) reveals that the activity concentrations of ^{226}Ra and ^{210}Pb, in scale samples, were as high as 2922 and 1794 Bq g^{-1}, respectively. Self-attenuation correction factors were estimated in another work (Al Attar et al., 2014) by transmission measurements using a ^{152}Eu point source and found to reach 5.08 for the most dense scale samples at gamma energy line of 45.5 keV.

In this study, an extensive effort was made to prepare a number of *home-made comparison* samples for elemental characterisation of scale samples by EDXRF. Correlation of elemental composition to density of scale samples, self-attenuation correction factors and radionuclide concentrations was investigated in detail. Finally, an approach was made to optimize the value of self-attenuation correction factors for the determination of the radioactivity concentration of ^{210}Pb in scale samples by gamma measurements.

2. Materials and methods

2.1. Scale sampling and preparation

A total of 32 scale samples were collected from a number of drums that are kept at the interim storage site of NORM decontamination facility (NDF) of Al Furat Petroleum Company, i.e. 500 km to the northeast of Damascus. The drums were chosen to cover the entire recorded range of the measured gamma dose rates (at contact, using Rados 110), i.e. 1–700 μSv h^{-1}. Sampling was carried out, in duplicate or triplicate, using a pressurised-stainless steel Auger (inner diameter of 8 cm) along the centre of the drum. Each sample, weighted *ca.* 80–120 g, was double-bagged in plastic and tightly sealed to ensure secure containment.

The scale samples were then transported to the laboratory, air-dried, ground and homogenised. Samples were divided into two halves. One half was used to determine the elemental composition using EDXRF as described later. The other half was dissolved according to the protocol mentioned in an earlier work (Al Attar et al., 2015b) and then counted *via* HPGe gamma spectrometry after 4 weeks to allow establishment of secular equilibrium between ^{222}Rn and progeny.

2.2. Sample preparation for elemental analysis

At present, there is no reference material available with specified concentration of chemical elements for NORM-scales (Landsberger et al., 2013). Hence, it was important to prepare so called "*home-made comparison samples*" using grade-reagent anhydrous inorganic salts, i.e. $CaCO_3$, Na_2CrO_4, Fe_2O_3, $ZnCl_2$, $Sr(NO_3)_2$, $BaSO_4$, $PbSO_4$, Na_2SO_4, K_2CO_3, and SiO_2. Six *home-made comparison samples* were prepared by weighing an aliquot mass of the appropriate salt (Table 1), that were dried overnight at 40 °C in the oven (Carbolite, England), ground by a mechanical mill (Fritsch, Germany), sieved through 185 μm (Retsch, Germany) and homogenised using Turbula mixer (Basel, Schweiz) for 48 h. About 2 g of the fine powder were then pressed into a pellet (of 2 cm diameter) using hydraulic press (MP 250 Massen GmbH, Germany) at 15 tonne. Each pressed pellet was finally covered by a Mylar foil and placed into a polyethylene cup of 4.91 cm^2. The scale samples were prepared in the same manner.

2.3. EDXRF measurements

The EDXRF used for elemental analysis was TX-2000 spectrometer (Ital structures, Italy) equipped with a Si(Li) semiconductor detector, with an energy resolution of 160 eV at 5.9 keV. Excitation of K_α and L_α-lines (in the case of Ba and Pb), within the energy range 3.3–16 keV, was generated by a 2 kW Mo-tube operated at a current of 20 mA and 35 keV voltage. Spectra were collected for 500 s live-time and analysed using QXAS-AXIL (Quantitative X-ray Analysis System and Analysis of X-ray spectra by Iterative Least square fitting) package (version 3.6), designed by the International Atomic Energy Agency (IAEA, 2007).

Precision and accuracy of the analysis technique were estimated by preparing five replicates of each *home-made comparison sample*. The theoretical and the measured concentrations mean (in % mass) of elements studied in the six samples are shown in Table 2; triple measurements were performed for each of the five replicate samples. The remaining matrix components were oxygen, sulphur and smaller amounts of various other elements (Table 3).

2.4. Correlation of the chemical composition of scale samples with self-attention correction factors

When a gamma photon passes through a sample it undergoes interactions, within the sample itself, that reduce the γ-rays reaching the detector, this effect is refereed as self-attenuation. The degree of self-absorption/attenuation depends on material density, elemental composition and gamma-ray energy (Cutshall et al., 1983; Kitto, 1991). In recent studies (Al Attar et al., 2014, 2015a), the activity concentrations of ^{210}Pb and ^{226}Ra in scale samples and self-attenuation correction factors for gamma emitters (i.e. C_f, see equation (1)) were determined *via* a transmission method using a ^{152}Eu point source. Herein, the effect of the elemental composition of scale samples on the activity concentration of the radionuclides and C_f values was investigated in detail. Statistical approaches *viz.* principal component analysis (PCA) and analysis of variance (ANOVA) were applied using XLSTAT Programme (2014).

$$C_f(E) = \frac{1 - (I/I_0)}{ln(I_0/I)} \tag{1}$$

where $C_f(E)$ is the self–attenuation correction factor for the efficiency at a particular γ-energy, I and I_0 are the attenuated and unattenuated photon intensities, respectively.

2.5. Optimising the estimation of self-attenuation correction factor of scale samples at 46.5 keV

To achieve better estimation of self-attenuation correction factors for radiochemical characterisation of scale by gamma spectrometry, scale samples were totally dissolved according to the protocol stated in a previous work (Al Attar et al., 2015b). This eliminated the effect of elemental composition and gave the