



Recovery of NORM from scales generated by oil extraction



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ABSTRACT

Scales, containing naturally occurring radioactive materials (NORM), are a major problem in oil production that lead to costly remediation and disposal programmes. In view of environmental protection, radio and chemical characterisation is an essential step prior to waste treatment. This study focuses on developing of a protocol to recover ^{226}Ra and ^{210}Pb from scales produced by petroleum industry. X-ray diffractograms of the scales indicated the presence of barite–strontium ($\text{Ba}_{0.75}\text{Sr}_{0.25}\text{SO}_4$) and hokutolite ($\text{Ba}_{0.69}\text{Pb}_{0.31}\text{SO}_4$) as main minerals. Quartz, galena and $\text{Ca}_2\text{Al}_2\text{SiO}_6(\text{OH})_2$ or sphalerite and iron oxide were found in minor quantities. Incineration to 600°C followed by enclosed-digestion and acid-treatment gave complete digestion. Using ^{133}Ba and ^{210}Pb tracers as internal standards gave recovery ranged 87–91% for ^{226}Ra and ca. 100% for ^{210}Pb . Radium was finally dissolved in concentrated sulphuric acid, while ^{210}Pb dissolved in the former solution as well as in 8 M nitric acid. Dissolving the scales would provide better estimation of their radionuclides contents, facilitate the determination of their chemical composition, and make it possible to recycle NORM wastes in terms of radionuclides production.

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1. Introduction

In the exploration and extraction of oil and gas, naturally occurring radioactive materials (NORM), from ^{232}Th and ^{238}U series may concentrate and accumulate as scale, sludge and produced water. Radium, the predominant radionuclide, can either stay in produced water or co-precipitate with barium forming complex sulphate compounds, carbonates and silicates. ^{210}Pb is also found in considerable concentrations. Only minute quantities of uranium and thorium may exist in sludge and scales due to their relative insolubility (Al-Saleh and Al-Harshan, 2008; El Affi and Awwad, 2005; Gazineu et al., 2005; Gazineu and Hazin, 2008; Smith, 1997). Scales restrict oil production and facilitate corrosive processes, causing in turn shutdowns for cleaning and frequent maintenance work (El-Hattab, 1985; Gazineu et al., 2005). Removing scale is a common practice in the oil industry and can either be performed mechanically or chemically. The use of scale inhibitors reduces the formation of scales (Morris and Paul, 2004; Omar et al., 2004). However, descaling operations give rise to scale waste, which contain in addition to NORM corrosion products, congealed oil and heavy metals (Al-Masri and Aba, 2005; Gazineu et al., 2005). Consequently, scales may cause health risk to workers during the

periodical maintenance and cleaning operations in addition to environmental pollution due to possibility of leaching and contamination upon storage in plastic drums, which is not recommended as an ultimate solution.

Worldwide, there are several methods practised for the treatment and remediation of sludge and scales produced from the oil industry. For instance, subsurface disposal, incineration or combustion in term of volume reduction (Abu et al., 2000; Mohamad Puad and Muha Noor, 2004), returning to the origin (abundant wells) (IAEA, 2004), and recycling and leaching using chemical solutions (Chau and Chrusciel, 2007; El Affi et al., 2009; Mola et al., 2013).

In this respect, an accurate determination of the activity of radionuclides in scale samples is an essential tool for waste management and environmental protection. However, radio-characterisation of scales would be a challenging task since they contain high concentrations of radionuclides with high specific activity, have complex matrix composition and high density. Correction for gamma attenuation in the waste matrix is usually performed by methods like density estimation or calculation of correction factors (Al Attar et al., 2014; Barros and Pecequilo, 2013; Celiktas, 2011; Jalali and Mohammadi, 2008; McMahon et al., 2004; San Miguel et al., 2004). However, waste drums are often heterogeneous, and span a wide range of matrix composition and activity distribution. This in turn increases the uncertainty associated, which cannot be accounted for by standard correction procedures.

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Recently, a research programme has been commenced to treat and manage oil solid wastes that are kept in plastic drums into an interim storage to comply with the disposal options, beneficial reuse or environmental discharge limits. A primary study (Al Attar et al., 2015) revealed that the maximum activity concentrations of ^{226}Ra , ^{228}Ra and ^{210}Pb were found to be 2922, 254 and 1794 Bq g $^{-1}$, respectively.

In this work, emphasis is made to recover radionuclides contaminants in scales, mainly ^{226}Ra and ^{210}Pb , to minimize their radiological impact onto human and the Environment. No purification of radionuclides to remove chemical impurities is included. The generalised dissolving protocol may represent the footstep for recycling of NORM solid wastes in terms of low-cost radionuclides production which is a milestone in waste management strategy.

2. Experimental

2.1. Scale sampling and preparation

A total of 32 scale samples were collected from different drums at the interim storage of NORM Decontamination Facility (NDF) at Al Fourat Petroleum Company, i.e. 500 km to the northeast of Damascus. The measured gamma dose rate of the stored drums (at contact, using Rados 110, Rados Technology, Oy, Finland) was recorded and found to range 1–700 $\mu\text{Sv h}^{-1}$. The density of the scale samples ranged 1.04–3.08 g cm $^{-3}$ and their activity concentration and elemental composition were determined in recent studies (Al Attar et al., 2015, 2016). Sampling was carried out, in duplicate or triplicate of each drum, using a pressurised-stainless steel Auger (inner diameter of 8 cm) along the centre of the drum. After spreading the sampled core on a polyethylene sheet, 20 g from each 10 cm of the core was taken and mixed, forming a representative sample of final weight ca. 80–120 g. Each scale sample was double-bagged in plastic and tightly sealed to ensure secure containment. It is worth pointing out that the scales were of various physical properties (colour, density and hardness) due to the volatilisation of hydrocarbon compounds upon storage. The scale samples were then transported to the laboratory, air-dried, ground and homogenised using Turbula mixer (Basel/Schweiz) for 24 hours.

A dust mask, disposal gloves and coveralls, glasses, helmet and heavy boots were used as personal protection equipment (PPE) during the sampling work, to comply with the Health Safety Legislations in the oilfields. Workers external exposure dose (measured via TLD films) throughout the entire study did not exceed the dose limit, i.e. 20 mSv y $^{-1}$.

2.2. Mineralogical analysis of scale samples

X-ray powder diffraction patterns (XRD) of the scale samples were scanned, at ambient temperature, over the angular range (2 θ) 15–50 $^\circ$, with a linear position sensitive detector (PSD), step of 0.5 $^\circ$ and counting time of 0.5 s step $^{-1}$. Stoe Transmission diffractometer used (Model STADI-P) was of monochromatic Cu-K $_{\alpha 1}$ radiation, $\lambda = 1.54060 \text{ \AA}$, selected with an incident beam curved-crystal germanium Ge(111), generated in a tube operating at 30 mA current and voltage of 50 kV.

2.3. Dissolving procedure of scale samples

2.3.1. Chemicals

^{133}Ba tracer, with nominal activity of 200 kBq in 0.1 M HNO $_3$ (reference date 18th March 2008), was supplied by Isotrak (IAEA, Austria). A tracer of ^{210}Pb with activity of 20.01 kBq in 1 M HNO $_3$ and 10 $\mu\text{g mL}^{-1}$ carrier of Pb(NO $_3$) $_2$ (reference date 15th Jan. 2004) was obtained from Isotope Products Laboratories (California, USA).

Chemicals used were analytical grade reagents and provided from commercial suppliers without further purification.

2.3.2. Dissolving procedure

Four (out of 32) scale samples were chosen to undergo decomposition. These samples were representative of the main two types observed by the XRD patterns (discussed later in detail) and covered the density range of the samples. It is well known that the matrix composition of such samples is very complex, thus duplicates and spiked experiments were performed in parallel.

An adequate weight of scale sample was placed on a ceramic crucible (KPM, Germany) and incineration was carried out at 600 $^\circ\text{C}$ for 4 hours using Carbolite (CWF 1200, England). The combustion permits the determination of percentage mass loss. After cooling, an aliquot weight of the ashen material (ca. 0.5 g) was transferred to a Teflon-lined vessel (PTFE, USA) and brought in contact with sufficient volume of an acidic medium, containing 5–6 mL of concentrated nitric acid (65%, Chem-Lab), 0–2 mL hydrochloric acid (37%, Merck) and 3–5 mL hydrofluoric acid (40%, Merck). High concentration of HF was necessary when the siliceous content exceeded 70% in the sample (EPA, 1996a). Stabilisation of Ba, Sb, Fe and Al in solution was made by concentrated HCl. The solid–solution mixture was then spiked with tracers, in particular with 200 μL of ^{133}Ba (1.232 kBq mL $^{-1}$) and 500 μL of ^{210}Pb (1.607 kBq mL $^{-1}$), to evaluate the radiochemical yield. The tightly closed Teflon vessel was accommodated in 45 mL acid digestion bomb (Parr, USA) which was introduced into a pre-heated oven at 250 $^\circ\text{C}$ for 2 hours. The bomb was carefully opened when cooling to room temperature. The mixture was, next, transferred to a cleaned PTFE-Teflon beaker.

Removal of excess hydrofluoric acid was achieved by gentle dryness of the component with successive additions of fresh concentrated nitric acid. Elements that form insoluble fluorides, such as Al, Ba, Ca and Mg, can be dealt with effectively by adding 1 g of boric acid and mildly re-heating for 1 hour. In some cases, hydrogen peroxide (30%, BDH) was added, with caution, to help oxidizing the organic content completely. Later, the solid obtained was treated with 20 mL of diluted nitric acid (8 M) and continuously stirred for 1 hour to ensure repining. Finally, the supernatant was filtered via Whatman–42 filter paper and washed with 5 mL of 8 M HNO $_3$. The filtrate was made up to the appropriate geometry for gamma counting, and designated as part-A. The remaining solid was washed with deionised water to remove residual solution and heated to near dryness; afterwards, 25 mL of concentrated sulphuric acid (98%, Merck) was added and left with stirring to complete dissolution of Ba(Ra)SO $_4$. The solution obtained was made up to the appropriate geometry for gamma counting, and designated as part-B. The layout of the generalised dissolving protocol is illustrated in Fig. 1.

2.3.3. Gamma measurement

The activity concentration of ^{210}Pb was determined at 46.5 keV (4.25%) and ^{226}Ra at 186.5 keV (3.51%) with no interference would occur by ^{235}U because uranium concentration is very low in comparison to radium in oil-production waste due to the insolubility of its compounds (Al-Masri et al., 2004; Gazineu et al., 2005; Gazineu and Hazin, 2008). ^{133}Ba was determined at 356 keV (62%). Gamma spectroscopy used was N-Type HPGe detector (Bruker Company, with relative efficiency of 60% and FWHM of 0.89 and 2.0 keV at 122 and 1332.5 keV, respectively). Estimation of the activity concentration of the studied radionuclides was performed, with an acquisition live-time of 1000 s, for each sample, using the following equation (IAEA, 2004):

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