

**NORM BASELINE STUDIES AND SURVEYS FOR THE E&P INDUSTRY**

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**Abstract**

Naturally Occurring Radioactive Material (**NORM**) baseline studies and surveys should be based on knowledge, where the deposits containing enhanced concentrations of Naturally Occurring Radionuclides (**NOR's**) are likely to be observed. The reliability of the outcomes of such studies or surveys are dependent on the determination of the activity balance between import and export streams from the facilities in a process oriented and systematic manner. Besides, gas/oil Exploration and Production (**E&P**) operating companies should be advised on 'routine NORM' surveillance, particularly with respect to 'NORM' sampling points and 'NORM' sampling and procedures relevant for their facilities. Collected samples should be analysed by means of validated, NORM- and cost-efficient methods. An example of a NORM survey is presented.

**Introduction**

The presence of natural radioactivity in oil and gas fields has been recognised world-wide and is exploited by petrophysicists as a means of identifying hydrocarbon bearing formations for almost half a century. This radioactivity is mainly due to the presence of potassium, but it can also result from the occurrence, both in formation rocks and specific ores, of isotopes from the uranium and thorium decay series. As a result of oil and gas production, radioactive "daughter" elements from the primordial "parent" nuclides  $^{238}\text{U}$  and/or  $^{232}\text{Th}$  may be transported from the formation to the production/treating facilities.

These NOR's include the radium isotopes ( $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{224}\text{Ra}$ ),  $^{222}\text{Rn}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ , which may build up in products, by-products and waste streams originating from the production and/or treatment of natural gas (**NG**), natural gas liquids\* (**NGL**), hydrocarbon condensate\*\* and crude oil. Also installations, pipelines, storage tanks and other equipment may become contaminated when the NOR's are deposited, either in (hard or soft) scales, sludges or as nearly invisible films. These contaminated materials are commonly denoted by the acronym NORM, but frequently also the acronym **TENORM** (Technologically Enhanced NORM) is used. Focusing on the main waste stream, also the term **LSA** (Low Specific Activity) scale/sludge is used.

The presence of NORM in installations may cause enhanced  $\gamma$ -radiation levels near and inside installations, whereby during a maintenance stop there is an additional health risk, if NORM would be inhaled or ingested. An extensive review on the encounter of NORM in products, by-products and waste stream from the E&P industry has recently been issued<sup>1</sup>. As neither the top of the  $^{238}\text{U}$ -series ( $^{238}\text{U}$  till  $^{230}\text{Th}$ ), nor the top of the  $^{232}\text{Th}$ -series ( $^{232}\text{Th}$ ) is present in technologically enhanced concentrations, E&P (TE)NORM is fully characterised by analysing for E&P product/waste streams for specific NOR's (Table 1).

\* NGL are those portions of reservoir gas that are liquefied at the surface in lease separators, field facilities, or gas processing plants. NGL include - but are not limited to - ethane, propane, etc., natural gasoline and hydrocarbon condensate.

\*\* Hydrocarbon condensates exist in the formation either as a liquid or as a condensable vapour. Liquefaction of gaseous components of the condensate usually occurs with reduction of well-fluid temperature to surface operating conditions.

**Table 1: Potential Appearance of NOR's in Product and Waste Streams of the E&P Industry**

<sup>238</sup> U-series	<sup>232</sup> Th-series	Product/Waste Stream
<sup>226</sup> Ra		production water, scale (scrapings, debris), sludge
<sup>222</sup> Rn		NG & C <sub>2</sub> , C <sub>3</sub> , C <sub>4</sub> ex NGL processing
<sup>210</sup> Pb		production water, scale (scrapings, debris), sludge
<sup>210</sup> Po		NGL & hydrocarbon condensate
	<sup>226</sup> Ra	production water, scale (scrapings, debris), sludge
	<sup>224</sup> Ra / <sup>226</sup> Th	production water* / scale* (scrapings, debris), sludge*

Based on table 1 and accurate processing knowledge of the gas/oil production/treatment facilities, the product/waste streams - in which NOR's may be present - and the spots - where TENORM might be deposited - can be assessed. Such an assessment is the basis for a survey for the presence of (TE)NORM inside the facilities. The outcomes of a (TE)NORM survey ultimately determines the precautionary health and safety measures to be taken on site, prior to the opening of installations. This also assists in the prevention of uncontrolled dispersal of (TE)NORM into the environment, be it via product- or waste streams or due to normal (operational, maintenance or inspection) procedures. This paper shortly describes the basics of a (TE)NORM survey, which are demonstrated at the hand of published case study

### (TE)NORM Surveys

In a (TE)NORM (baseline) survey, for the two conditions (operation/stop) of a facility two distinct phases can be distinguished:

#### 1. operating conditions

- a) an external survey on accessible vessels, flow lines, valves and other equipment on the presence of penetrating  $\gamma$ -radiation, using an intrinsically safe detection system;
- b) sampling of continuous product (NG, NGL, hydrocarbon condensate) and waste (production water, glycol) streams at pre-installed sampling points;

#### 1. maintenance stop

- b) an internal survey of vessels or other bulky equipment for the presence of (less) penetrating  $\gamma$ -radiation, using a detection system, which is preferably intrinsically safe and has a wide  $\gamma$ -photon energy response (40 keV <> 2 MeV), or an  $\alpha/\beta/\gamma$ -contamination monitor on the basis of a permit-to-work system, and
- c) grab sampling of deposits, scales, sludges and other waste streams from vessels or other equipment, which are opened during the stop period.

Step 1a) may lead to identification of spots in the facilities, where radium LSA deposits or high <sup>222</sup>Rn concentrations might be present. As the external detection of LSA material present inside the facilities depends on various factors, i.a. the activity concentration (Bq/g); the total mass of the deposit/stream and its distribution (e.g. at bottom of or homogeneously distributed over the inner surface of a flow line) of this mass in the 'field-of-view' of the detector; the elemental composition and specific density of the deposit/stream, the elemental composition and wall thickness of the installation part, and the total distance of the 'radiation source' to the monitor. From this list it is clear, that at least some degree of standardisation of radiation monitoring is required (e.g. agreement with respect to distance between monitor and facility). As most of this information will be unknown beforehand, it is needless to say that from any externally measured  $\gamma$ -radiation level no quantitative information on the NOR concentration of the deposits can be obtained. Basis on 'typical' low pressure E&P parameters a detection limit of 200 Bq[<sup>226</sup>Ra+<sup>226</sup>Ra]/g is estimated. Consequently, the absence of enhanced radiation levels near facilities does not warrant the absence of NORM below regulatory concern.

\* <sup>224</sup>Ra ( $t_{1/2}$  = 3.6 days) may only appear "unsupported" in fresh production waters. When present in LSA scale/ sludge, it is stemming from ingrowth from <sup>226</sup>Ra via <sup>228</sup>Th. From a radiological point of view it is more adequate to quote the <sup>228</sup>Th (more radiotoxic, also only present by ingrowth) concentration for scale/sludge.

Samples taken in step 1b) are used for identification of NOR's and sensitive quantification of their concentrations. As both sampling and analysis technique strongly influence the quantitative results, standardisation - both for sampling and analysis - is essential. Several 'standardised' sampling procedures have been issued. Upon sending homogenised E&P samples to various contractor laboratories, however, the analysis results quoted scattered severely<sup>3,4</sup>. By agreeing on critical steps in the analytical protocol, the results obtained by most contractor laboratories were identical. This stresses the need for quality assurance procedures in contracting independent laboratories for E&P NORM analysis. The most cost/time-effective analytical methods<sup>3,4</sup> are: Lucas  $\alpha$ -scintillation cells for determination of  $^{222}\text{Rn}$  in NG (det. limit  $\approx 10 \text{ Bq/m}^3$ , standard temperature and pressure, STP),  $\gamma$ -spectrometry for determination of radium isotopes,  $^{210}\text{Pb}$  and  $^{228}\text{Th}$  in all kind of E&P samples ( $\approx 0.02 \text{ Bq/g}$ ) and  $\alpha$ -spectrometry for determination of  $^{210}\text{Po}$  in all kind of E&P samples ( $4 - 0.004 \text{ mBq/g}$ ).

Step 2a) is required for the determination of the  $\gamma$ -radiation field inside equipment to assess external radiation doses to maintenance personnel and to assess, if any (TE)NORM is present. As equipment is generally flushed before entry, in this case enhanced  $\gamma$ -radiation fields inside equipment are caused by radium isotope progeny and/or by  $^{210}\text{Pb}$  containing deposits. Due to the pre-defined  $\gamma$ -energy response a  $\gamma$ -radiation monitor (intrinsically safe/permit-to-work) may be able to detect  $^{210}\text{Pb}$ . Detection limits will be lower than for step 1a), but the absence of enhanced  $\gamma$ -radiation levels is still not yet a full guarantee for the absence of NORM below regulatory concern.  $\alpha/\beta/\gamma$ -Contamination monitors are much more sensitive than  $\gamma$ -radiation monitors, but both  $\alpha/\beta$  self-absorption phenomena and the occurrence of unrelated  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}/^{228}\text{Th}$  and  $^{210}\text{Pb}$  concentrations prevent both NOR identification and the quantitative determination of NOR concentrations.

The ultimate proof for NORM below regulatory concern is the acquirement and analysis of samples from the inside of installations (step 2b)). Samples from inside installations are generally obtained by grab sampling of deposits or scraping/wiping of surface contaminated areas. The sample material can be quantitatively analysed by the aforementioned  $\gamma$ - and  $\alpha$ -spectrometric methods<sup>3,4</sup>. However, the actual reliability of the quantitative results is mainly determined by the way, in which the samples have been acquired. Therefore, it is essential to provide this information, when quoting NOR concentrations.

#### Case Study - NORM in NG/NGL Treating Plants

- the noble gas  $^{222}\text{Rn}$  emanating from reservoir material, is transported ('partitioning') with NG, with NGL or with crude oil to surface facilities. Though in substantial lower concentrations  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  have also been observed in NG. The reported concentration range of these three NOR's in NG<sup>1</sup> varies from 0.005 to 200 kBq[ $^{222}\text{Rn}$ ]/m<sup>3</sup>, 0.005 to 0.02 Bq[ $^{210}\text{Pb}$ ]/m<sup>3</sup> and 0.002 to 0.08 Bq[ $^{210}\text{Po}$ ]/m<sup>3</sup> at STP. The  $^{222}\text{Rn}$  concentration in the NG associated with NGL for the plant<sup>5</sup> under consideration is 2.3 kBq/m<sup>3</sup>, STP.
- upon separation of methane ( $\text{CH}_4$ ) from the other hydrocarbon constituents of NG/NGL,  $^{222}\text{Rn}$  becomes concentrated in the NGL fraction, consisting of ethane ( $\text{C}_2\text{H}_6$ ; abbreviated  $\text{C}_2$ ), propane ( $\text{C}_3\text{H}_8$ ;  $\text{C}_3$ ), butane ( $\text{C}_4$ ) and gasoline (pentane and heavier hydrocarbons;  $\text{C}_5+$ ). During fractionating of NGL with main constituents below  $\text{C}_5+$ ,  $^{222}\text{Rn}$  concentration factors of about 20 (gas volume base) in the  $\text{C}_3$  fraction have been observed<sup>1</sup>. Enhanced  $^{222}\text{Rn}$  concentrations in the  $\text{C}_2$  to  $\text{C}_4$  fractions are caused by the co-play of molecular shape of the  $^{222}\text{Rn}$  atom and the  $\text{C}_2$  to  $\text{C}_4$  molecular sizes, together with a similarity of the boiling points.

- encounter of unsupported\*  $^{222}\text{Rn}$  concentrations in production/treatment facilities leads to enhanced  $\gamma$ -radiation levels, due to the fast in-growth of short-lived  $^{222}\text{Rn}$  progeny (i.c.  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$ ). After stopping operations (the influx of  $^{222}\text{Rn}$  is stopped), the  $\gamma$ -radiation level decreases according to the 3.8 days half-life of  $^{222}\text{Rn}$ . In the case of venting the equipment (dispersal of  $^{222}\text{Rn}$  into the atmosphere), the  $\gamma$ -radiation level decreases with an apparent half-life of about 40 minutes. In NGL processing units, external radiation levels in filters of up to  $35\ \mu\text{Sv/h}$ , in NGL pumps of up to  $200\ \mu\text{Sv/h}$ , in  $\text{C}_3$  storage tanks of up to  $60\ \mu\text{Sv/h}$  and in NGL/ $\text{C}_3$  shipping pumps,  $\text{C}_3$  reflux pumps, elbows, flanges etc. of up to  $2.8\ \mu\text{Sv/h}$  have been reported<sup>1</sup>. Another aspect of the high  $^{222}\text{Rn}$  concentrations is surface contamination of equipment and generation of deposits contaminated with long-lived  $^{222}\text{Rn}$  progeny (i.c.  $^{210}\text{Pb}$ ,  $^{210}\text{Bi}$  and  $^{210}\text{Po}$ ). As long-lived  $^{222}\text{Rn}$  progeny emits  $\alpha$ - and  $\beta$ -radiation, it can be of substantial importance with respect to internal dosimetry.

#### External $\gamma$ -Radiation Monitoring during Operations

Polymer fouling was suspected in the de-propaniser and de-butaniser towers of the ethylene plant<sup>5</sup> and a contractor was called in to carry out a  $\gamma$ -transmission scan. During these scans radiation levels (due to strongly enhanced  $^{222}\text{Rn}$  concentrations in liquid  $\text{C}_3/\text{C}_3^+$  and  $\text{C}_4/\text{C}_4^-$  present at the distillation trays) as high as twice the calculated intensity were observed. Consequently, step 1a) of the NORM survey was carried out and revealed enhanced  $\gamma$ -radiation levels over all over the processing site, but in particular close to the de-propaniser and de-butaniser towers (up to  $9\ \mu\text{Sv/h}$ ). At a similar site<sup>6</sup> a propylene fractionator showed  $\gamma$ -radiation levels of about  $2\ \mu\text{Sv/h}$ , while the fractionator reflux pumps showed levels up to  $10\ \mu\text{Sv/h}$ .

#### Sampling Product Streams during Operations

During operations the product ( $\text{C}_2$ ) stream and one by-product ( $\text{C}_3$ ) stream has been sampled (step 1b)):  $\text{C}_2$  separated from the NG/NGL stream<sup>5</sup>, contains  $3 - 18\ \text{kBq}[^{222}\text{Rn}]/\text{m}^3[\text{C}_2]$  at STP, while the  $\text{C}_3$  fraction, which on its turn was separated from the  $\text{C}_2$  fraction, was even much higher being  $150 - 380\ \text{kBq}[^{222}\text{Rn}]/\text{m}^3[\text{C}_3]$ , STP.

#### $\gamma$ -Radiation / $\alpha/\beta/\gamma$ -Contamination Monitoring inside Fractionators

Unfortunately the outcomes of step 2a) were not reported<sup>5</sup>. After stopping operations inside a propylene fractionator at a similar site<sup>6</sup>, inside the manhole only background  $\gamma$ -radiation fields could be measured, while  $\alpha/\beta/\gamma$ -contamination monitoring showed enhanced levels inside the manhole (up to 31,000 counts per minute - cpm) and wipe tests showed up to  $500\ \text{cpm}[\alpha]$  and  $9500\ \text{cpm}[\beta]$ . Most likely for the  $\gamma$ -radiation measurements a monitor not capable of detecting the low energy (46 keV)  $\gamma$ -photon emitted upon  $^{210}\text{Pb}$  decay has been used. Consequently only background  $\gamma$ -radiation levels are measured.

#### Sampling Deposits and Product Streams during operations

The outcomes of step 2b) of the NORM survey for the ethylene plant under consideration<sup>5</sup> are summarised in Table 2. Most likely the  $^{210}\text{Po}$  contamination is just generated from  $^{210}\text{Pb}$  decay through  $^{210}\text{Bi}$ . Consequently,  $^{210}\text{Po}$  concentrations are supported by  $^{210}\text{Pb}$  decay and can never exceed  $^{210}\text{Pb}$  concentrations.

\*  $^{224}\text{Ra}$  ( $t_{1/2} = 3.6$  days) may only appear "unsupported" in fresh production waters. When present in LSA scale/ sludge, it is stemming from ingrowth from  $^{226}\text{Ra}$  via  $^{228}\text{Th}$ . From a radiological point of view it is more adequate to quote the  $^{228}\text{Th}$  (more radiotoxic, also only present by ingrowth) concentration for scale/sludge.

**Table 2: Observed equipment surface contamination in NGL processing plant<sup>5</sup>**

System	Equipment	Surface Contamination*		
		Bq[ <sup>210</sup> Pb]/cm <sup>2</sup>	Bq[ <sup>210</sup> Pb]/g	Bq[ <sup>210</sup> Po]/cm <sup>2</sup>
De-ethaniser	Reflux drum	5.5	29.3	
	Tower	0.26	8.2 - 8.6	
	Reboilers	0.14 - 0.3		
	C <sub>3</sub> Recycle exchanger		8.9 - 31.3	
	Upper feed vaporiser	0.18 - 1.93	18.3	
	PSV's	2.4		
	Overhead condenser	0.04 - 0.18		
De-methaniser	Tower			0.17 - 0.47
De-propaniser	Tower	4.53	184.7	
	Reflux drum	17.7	76.4	
	Reboiler	1.5 - 2.7	106 - 174	
	Recycle/product pumps	1660		
	PSV's	2.5 - 4.6		
De-butaniser	Tower	0.24 - 2.42	0.3 - 234	
	Reboilers	0.27 - 0.54	9.7 - 52.9	
	Bottom cooler	2 - 4	24.6	
	Bottom filters	1.1	4.8	
	Condenser / Reflux drum	Background		
Propene refrigeration	Compressor			0.11 - 0.36
	3rd section economiser	1.16		
	H.P. economiser	1.3 - 2.0		
	Refrigeration condenser			0.11 - 0.37
	Refrigeration accumulator	0.19		
C <sub>3</sub> transfer and storage	Transfer pump	116 - 596		
	Product sphere	5.3 - 18.8		
	Rail loading arm	11.4 - 23.2		

## References

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\* For hard to remove ('plating') contamination Bq/cm<sup>2</sup> is used, while for easy to remove ('polymeric deposits') contamination Bq/g is used.