



**NATURAL RADIOACTIVITY IN MINING AND HYDROCARBON
EXTRACTION INDUSTRY**

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SUMMARY

Natural radioactivity is a well known phenomenon which can be produced by variable concentrations of uranium and thorium series radionuclides in water, soils, minerals, etc..

In this paper the following mining and hydrocarbon extraction plants are particularly taken into account as examples of possible radioactivity accumulation which can cause radiation protection problems: a) industries using Zircon sands to produce refractory and ceramic materials (U, Th); b) phosphorites manufactory to prepare phosphoric acid, phosphogypsum and fertilizers (U, Ra); c) hydrocarbons extraction and treatment processes where a formation of low specific activity (L.S.A.) scales and sludges can be produced (U, Th, Ra).

The relevant results and the possible radiation protection risks for the professional exposed staff are reported. A special emphasis is given to some African phosphorites (Boucras, Togo, Morocco) and L.S.A. scales (Tunisia, Congo, Egypt).

Keywords: Natural Radioactivity, Zircon Sands, Phosphorites, L.S.A. scales.

1. INTRODUCTION

Generally speaking the radiological hazard connected to natural radioactivity is not so important: however some radiation protection problems can occur in particular industrial processes involving the treatment of large quantities of slightly radioactive materials. In these cases a high concentration of radioactive substance (NORM: Naturally Occurring Radioactive Materials) can be found in special points of the plant, in the manufacture

by-products and in the wastes. Sometimes the natural radioactivity concentration can be so high to rise radiation protection problems which can be assimilated in a sense to the ones faced in the presence, handling and disposal of non-sealed radioactive sources.

2. EXPERIMENTAL AND RESULTS

2.1. Determination of uranium and thorium in Zircon Sands

Zircon sands, essentially composed of zircon and baddeleyte, are materials used in Zirconium extraction industry, in foundry sands, in refractories and ceramics. Because of the high concentration of natural radionuclides these sands may represent a health problem for the exposed staff. Therefore it is necessary to determine the radioactivity level due to U and Th isotopes in these materials. An extraction chromatography method (1) with a column of 50+100 mesh microporous polyethylene (Microthene-710) supporting tri-n-octylamine (TNOA) was used to separate uranium and thorium from Zircon sands (Fig.1). The two elements were determined by fluorimetry and colorimetry respectively or by alpha spectrometry after electrodeposition.

Table 1 shows that the uranium and thorium percent concentrations, determined by alpha spectrometry taking into account the peaks of ^{238}U and ^{232}Th respectively, are in good agreement with those obtained by fluorimetric and colorimetric analysis (Arsenazo III). The alpha spectra showed that ^{238}U and ^{234}U were in secular equilibrium.

Tab.1: Uranium and thorium percent concentration (w/w) in Zircon Sands: comparison between different techniques

Sample number	Th		U	
	(colorimetry)	(α spectrometry)	(fluorimetry)	(α spectrometry)
1	0.022	0.018	0.021	0.025
2	0.021	0.022	0.023	0.024
3	0.016	0.016	0.023	0.025
4	0.019	0.019	0.020	0.023
5	0.016	0.017	0.024	0.022
5	0.022	0.019	0.029	0.023

2.2. Determination of uranium and radium in Phosphorites and their Industrial Derivatives

Phosphorites consist essentially of calcium phosphate and they are largely used as crude materials to prepare elemental phosphorus, phosphoric acid, phosphogypsum, phosphatic fertilizers, etc. Sometimes the uranium concentration in phosphorites is so high that its recovery is economically worthwhile. Therefore, it is of some interest to determine alpha emitter radionuclides either in the original material and in the derivatives (H_3PO_4 and CaSO_4) obtained after treatment with H_2SO_4 . As a matter of fact the knowledge of the alpha activity in the relevant steps of the industrial process permits to evaluate the radiation risk to the exposed workers.

An extraction chromatography method (2) based on Microthene supporting a solution of tri-n-octylphosphine oxide (TOPO) was used to separate uranium and radium from phosphorites and their industrial derivatives (Fig.2). Uranium was then determined by fluorimetry and by alpha spectrometry after electroplating, and radium by coprecipitation as $\text{Ba}(\text{Ra})\text{SO}_4$ and alpha counting with a $\text{ZnS}(\text{Ag})$ alpha detector.

Table 2 shows the uranium percent concentration (w/w) obtained by fluorimetry and by alpha spectrometry. The two results are in good agreement as far as the relevant errors are taken into account. The activity of the ^{238}U isotope is also reported.

Uranium concentration in phosphorites ranged between 0.006% (Giordania) and 0.011% (Morocco); these results are in good agreement with the ones obtained by gamma spectrometry with $\text{Ge}(\text{Li})$. The phosphorites alpha spectra showed that uranium isotopes (^{238}U , ^{235}U , ^{234}U) were in radioactive equilibrium. Uranium concentration in one sample of 30% H_3PO_4 (Boucraa) was about 0.005%: on the contrary it was not possible to detect uranium in phosphogypsum. This fact is due to the chemical process step with H_2SO_4 (precipitation of $\text{Ca}(\text{Ra})\text{SO}_4$) and to the formation of strong uranium phosphate complexes in the H_3PO_4 .

Table 3 shows that ^{226}Ra concentration in phosphogypsum is similar to that of phosphorite. As a matter of fact, after the chemical treatment, radium is present as $\text{Ca}(\text{Ra})\text{SO}_4$ in phosphogypsum and in some pipe slimes, and it is absent in H_3PO_4 .

If the results of table 2 and 3 are taken into account, it appears that ^{226}Ra in phosphorites was in radioactive equilibrium with ^{238}U .

Tab 2: Uranium concentration in phosphorites, H₃PO₄ and phosphogypsum

Sample	Percent Mean Concentration, (w/w)		²³⁸ U activity, kBq/kg
	Fluorimetry	Radiometry	
Morocco	0.0110±0.0014	0.0106±0.0009	1.32±0.11
Togo	0.0098±0.0013	0.0110±0.0009	1.37±0.13
Giordania	0.0060±0.0008	0.0075±0.0007	0.94±0.07
Boucraa	0.0075±0.0010	0.0070±0.0006	0.87±0.07
H ₃ PO ₄ 30% (Boucraa)	0.0049±0.0006	0.0053±0.0004	0.66±0.05
Phosphogypsum (Boucraa)	N.D.	N.D.	N.D.
Phosphogypsum (Togo)	N.D.	N.D.	N.D.

N.D. - not detectable

Tab. 3: Radium-226 concentration (3 measures)

Sample	Mean Concentration, kBq/kg
Phosphorite, Togo	1.27±0.19
Phosphorite, Boucraa	0.89±0.13
Phosphogypsum, Togo	1.28±0.19
Phosphogypsum, Boucraa	0.65±0.10
H ₃ PO ₄ 30%, Boucraa	N.D.

N.D. - not detectable

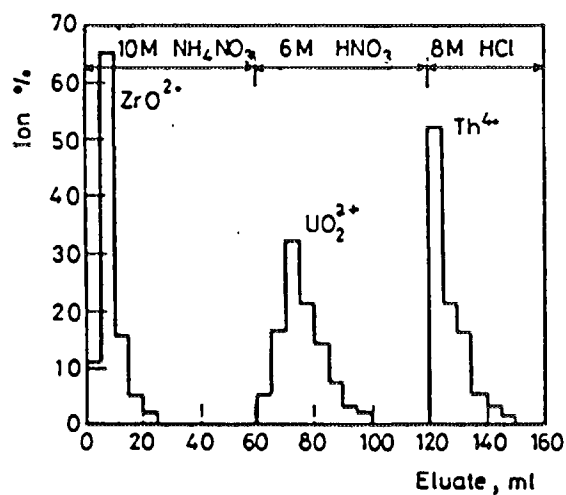


Fig.1: Elution diagram for the separation of uranium and thorium from zirconium by Microthene-TNOA column

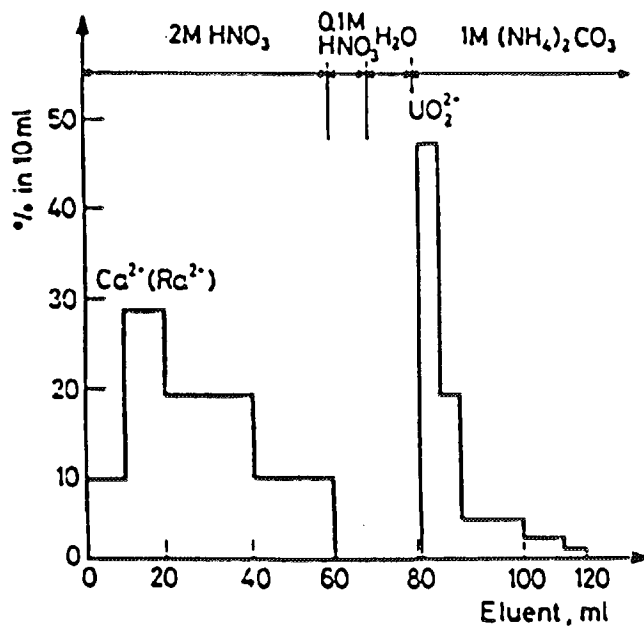


Fig.2: Elution diagram for the separation of radium and uranium in a phosphorite sample by Microthene-TOPO column

2.3. Radium, uranium and thorium determination in Low Specific Activity Scales of some oil and gas production plants.

Natural radioactivity due to uranium, thorium and radium compounds can be observed also in hydrocarbon reservoirs. In this case radioactivity traces are carried together with different extraction products so causing scales and sludges along the different plant lines (valves, pipes, separators, etc.). These scales reduce plant efficiency so hindering the extraction operation; furthermore, the radioactivity sources can cause also some radioprotection problems (3-6).

Scales production is due to the precipitation of alkaline earth metal sulphates and carbonates caused by solubility changes in the aqueous solution where they are present. Besides calcium, strontium and barium sulfates, scales can also contain some radionuclides, mainly radium, and in this case they are called "Low Specific Activity Scales" (L.S.A. scales).

Production plants L.S.A. scales present the following two radioprotection problems:

- a) a gamma irradiation risk to the staff remaining for a long time in some particular plants areas;
- b) a possible risk of internal radiocontamination to the staff involved in mechanical removal and disposal of scales. In these processes whisks are generally utilized with a consequent production of a fine powder, which can be inhaled or ingested. This being established, a program was started to evaluate the real concentration of uranium, thorium and ^{226}Ra in scales, sludges and waters of some Agip plants situated in Italy, Northern Sea and Africa ().

Uranium, thorium and radium were separated by Extraction Chromatography with a Microthene-TOPO column (Fig.3). Uranium and thorium were determined by alpha spectrometry after electroplating; ^{226}Ra was coprecipitated by $\text{Ba}(\text{Ra})\text{SO}_4$ and counted by a $\text{ZnS}(\text{Ag})$ detector.

The general survey involved 391 oil wells, 16 oil centers, 157 gas wells, 38 gas centers, 42 platforms and 10 fields used as natural tanks to store gases (6). However L.S.A. scales were found only in some plants, particularly in phase separators: probably this phenomenon can be caused by the strong temperature and pressure changes which fluid undergo when passing in these elements and also by the slow flow-rates which facilitate the formation of muddy scales; Table 4 shows the gamma dose rate values and the ^{238}U , ^{223}Th and ^{226}Ra concentrations measured where the scales have been located.

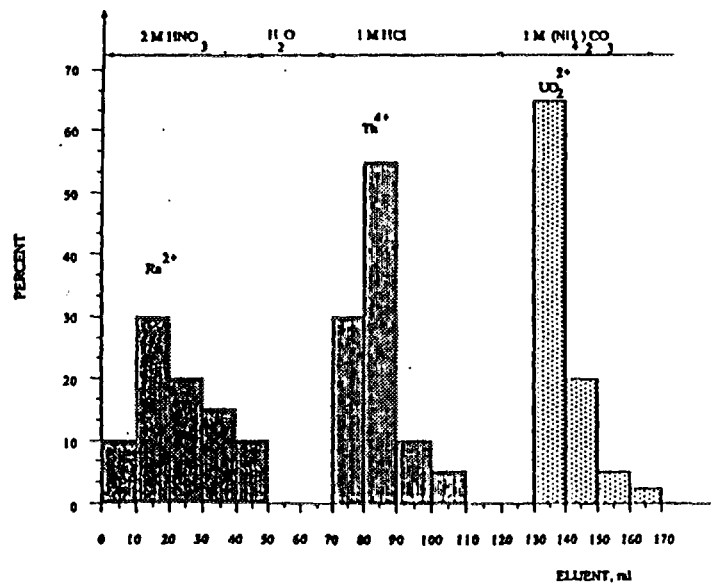


Fig.3: Elution diagram of Ra²⁺, Th⁴⁺ and UO₂²⁺ with a Microthene-TOPO column for L.S.A. scale sample

Tab.4: ²³⁸U, ²³²Th and ²²⁶Ra concentration in scales and external γ dose rate values.

Plant Features and Site	Extracted Hydrocarbon	Depth (km)	Concentration (Bq/kg)			γ Dose rate (μ Sv/h)
			²³⁸ U	²³² Th	²²⁶ Ra	
<i>Po valley, Italy</i>						
Extraction Plant	Liquid	6	<0.9	<0.8	2890 \pm 578	0.20
Extraction Plant	Liquid	5	<0.9	<0.8	1126 \pm 225	1.00
Extraction Plant	Mixed	5	<0.9	<0.8	120 \pm 24	0.10
Collection Plant	Gaseous	-	23.8 \pm 4.3	18.9 \pm 3.8	30 \pm 6	0.10
Collection Plant	Gaseous	-	53.8 \pm 10.8	<0.8	<2.7	0.17
<i>Southern Italy</i>						
Collection Plant	Liquid	-	11.3 \pm 2.3	<0.8	110 \pm 22	0.05
<i>Northern Italy</i>						
Off Shore Platform	Liquid	3	<0.9	<0.8	780 \pm 156	-
<i>Tunisia</i>						
Extraction Plant	Liquid	1	1.2 \pm 0.2	<0.8	189 \pm 238	0.25
Treatment Plant	Liquid	1	<0.9	<0.8	31 \pm 6	0.05
Phase Separation Plant	Liquid	1	7.6 \pm 1.5	5.1 \pm 1.0	64 \pm 12	-
<i>Congo</i>						
Phase Separation Plant	Liquid	1	<0.9	<0.8	97 \pm 20	0.01
Oil Storage Reservoir	Liquid	1	2.7 \pm 0.5	2.2 \pm 0.4	151 \pm 30	0.04

Taking into account these figures, the following remarks can be done:

1. ^{238}U and ^{232}Th concentrations were either non detectable or very low (collection and separation plants);
2. ^{226}Ra concentrations was higher in the oil extraction plant scales (800-3000 Bq kg⁻¹) than in other plants (300-400 Bq kg⁻¹); for any specific plant the ^{226}Ra concentration seemed to be directly correlated to the extraction depth.

As far as the correlation of ^{226}Ra concentration with the relevant external gamma dose rate is concerned, a fair accordance could be found for the African scales; on the contrary some discordances were found for the Italian scales. This fact can be due to the following reasons: a) the gamma dose rate is correlated not only to radium concentration, but also to the scale total amount; b) the variable deposition and detection geometry; c) the variable gamma adsorption due to the different materials thickness and density.

In all the analysed samples the principal uranium isotopes (^{238}U and ^{234}U) resulted in radioactive equilibrium; for the majority of samples ^{232}Th and ^{228}Th resulted in radioactive equilibrium too; however in some African scales the ratio $^{228}\text{Th}/^{232}\text{Th}$ reached a value up to 700. This fact is due to the presence of initially high concentrations of the parent ^{232}Th from which ^{228}Ra separated because of the different chemical behaviour of radium and thorium: in this case the internal radiocontamination risk is due to ^{228}Th and to its daughters (^{224}Ra , ^{212}Bi , ^{220}Rn , ^{216}Po , ^{212}Po).

The obtained results clearly show that the L.S.A. scales phenomenon does not present a heavy radiation protection problem for the plants management; as a matter of fact the staff presence around these plants is discontinuous (only a few hours per year), the gamma dose rates are low and only in a few cases the action levels (25 $\mu\text{Sv h}^{-1}$; 5 mSv y⁻¹) suggested by national and international radiation protection rules are exceeded (7).

The routine maintenance of plants presenting L.S.A. scales must be done taking into account the dose values in order to reduce as low as possible the contamination risk for the staff and the environment.

As far as carbonate L.S.A. scales are present it is sufficient to wash the pipes with hydrochloric acid; in the other cases (sulphates) a wet mechanical treatment must be done and the staff has to wear protective masks and clothes. some investigations are now in progress to correlate the oil fields geochemical features with the L.S.A. scales formation mechanisms and to set up suitable methods for the solubilization and the prevention of the scales.

A connected radiation protection problem is the L.S.A. scales disposal: the possibility of reinjection into the reservoirs will be seriously taken into consideration in the presence of easily soluble substances.

2.3.1. Radium, thorium and uranium concentration in samples of four Egyptian oil extraction Plants

Some water, oil, mud, soil and scale samples coming from Egyptian oil extraction Plants (Belahim, Ashraf, Aghar and Melliha) were also measured to calculate the ^{238}U , ^{232}Th and ^{226}Ra concentration. Table 5 shows the relevant results for the Belahim and Ashrafi Plants.

Tab. 5: ^{238}U , ^{226}Ra and ^{232}Th concentration in some samples of Belahim and Ashrafi Plants (Egypt).

Sample	Concentration (Bq/kg)		
	^{238}U	^{226}Ra	^{232}Th
BEL-1 (soil)	25.5±2.8	35.0±7.0	14.7±1.8
BEL-2 (soil)	26.8±2.9	160.0±32	18.8±2.1
BEL-3 (sludge)	4.8±0.8	19,000±3,800	N.D.
BEL-4 (scale)	N.D.	10,618±2,124	N.D.
BEL-5 (cont. soil)	22.0±4.2	21,307±4,260	N.D.
BEL-6 (soil)	22.5±3.1	24.4±5.0	12.7±1.6
BEL-7 (soil)	40.9±4.6	31.0±0.6	23.6±2.8
BEL-8 (water)	N.D.	3.0±0.6	N.D.
ASH-2 (water)	N.D.	85.0±17.0	N.D.
ASH-3 (mud)	N.D.	793.0±159.0	N.D.
ASH-6 (mud)	N.D.	2,043.0±410	N.D.
ASH-11 (oil)	N.D.	119.0±2.4	N.D.
ASH-13 (oil)	N.D.	N.D.	N.D.

N.D. - not detectable

Detection limits:

Soils, muds, sludges and scales:

^{238}U = 0.7 Bq/kg

^{232}Th = 0.9 Bq/kg

Oil:

^{238}U = 1.3 E-3 Bq/l

^{232}Th = 1.7 E-3 Bq/l

Water:

^{238}U = 6.6 E-4 Bq/l

^{232}Th = 4.3 E-4 Bq/l

When ^{226}Ra concentration was high (BEL-3, BEL-4, BEL-5) a great quantity of ^{228}Th was found (Fig.4) deriving from ^{228}Ra which also accumulates in the scales, sludges and muds.

The three radionuclides were measured also in five water samples of the Aghar Plant, but the concentration resulted to be lower than the relevant detection limits ($^{226}\text{Ra} = 2.3 \text{ E-}2 \text{ Bq/l}$; $^{238}\text{U} = 4.0 \text{ E-}4 \text{ Bq/l}$; $^{232}\text{Th} = 2.0 \text{ E-}4 \text{ Bq/l}$).

Finally three water samples of the Meleiha Plant were measured: only low concentration of ^{226}Ra could be detected ($2.1 + 3.4 \text{ Bq/kg}$)

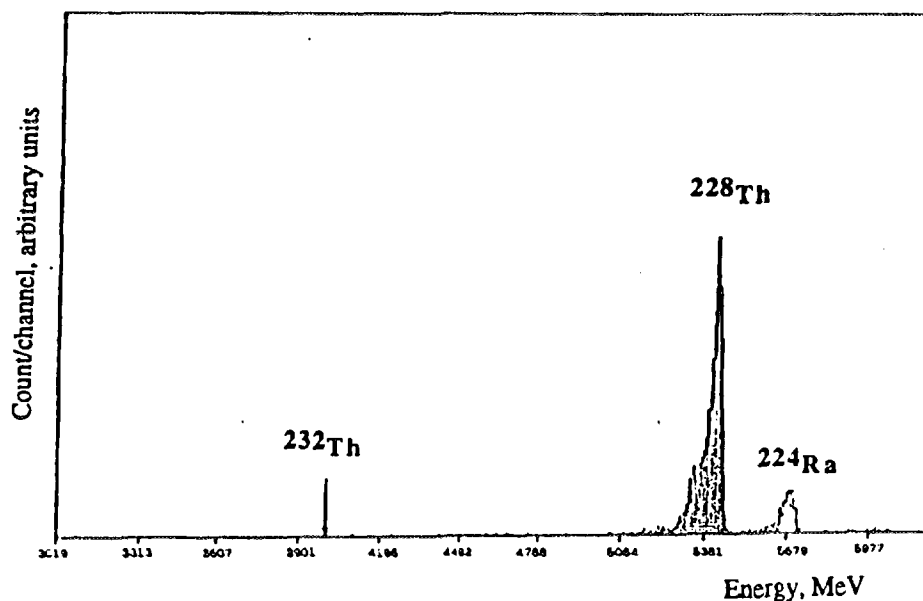


Fig.4: Alpha spectrum of thorium separated from a sample (BEL-3); the great concentration of ^{228}Th is due to the presence of ^{228}Ra which concentrates together with ^{226}Ra

3. CONCLUSION

The three examples taken into account in this paper clearly shows that in chemical industries and in hydrocarbon extraction plants an accumulation of natural radioactive isotopes can occur. ^{238}U , ^{234}U , ^{232}Th , ^{228}Th , ^{226}Ra , ^{228}Ra , ^{224}Ra can concentrate in particular steps of the industrial process, so causing radiation protection problems regarding the involved staff and the radioactive disposal.

As far as the radioanalytical method is taken into account, the separation techniques using extraction chromatography showed to be suitable to solve the problem; on the other and

alpha spectrometry gives important information about the chemical and radioactive equilibria or disequilibria.

Finally it has to be said that in some cases the natural radioactivity can be so high to exclude the use of particular industrial by-products which could cause a non justified gamma dose to the population.

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