

THE DETERMINATION OF RADIUM, URANIUM AND THORIUM IN LOW
SPECIFIC ACTIVITY SCALES AND IN WATERS OF SOME OIL AND
GAS PRODUCTION PLANTS

C. Testa, D. Desideri, M.A. Meli, C. Roselli
(General Chemistry Institute, Urbino University, Italy)

A. Bassignani, P.B. Finazzi
(Radiation Protection Institute, AGIP, Milan)

Abstract

Low specific activity scales consisting of alkaline earth metal carbonates and sulphates are often present in some gaseous and liquid hydrocarbon plants; these scales contain a certain concentration of radium, uranium and thorium which can cause a risk of gamma irradiation and internal radiocontamination when they must be mechanically removed. ^{238}U , ^{232}Th and ^{226}Ra were determined in scales, sludges and waters coming from different plants. ^{238}U and ^{232}Th concentrations were found very low; the isotopes ^{238}U and ^{234}U resulted in secular radioactive equilibrium, ^{232}Th and ^{228}Th were not always in equilibrium. ^{226}Ra concentration resulted to be higher in the scales and sludges than in waters.

Introduction

Naturally occurring radioactive materials are known to be present in different concentrations in oil and gas production plants giving rise to the so called Low Specific Activity (L.S.A.) scales (1-3).

The chemical composition of L.S.A. scales varies, consisting mainly of alkaline earth metal sulphates and calcium carbonates incorporating small amounts of radium (1); uranium and thorium can also be present in some extent; the scales production is due to different causes: injection of incompatible waters (75%), evaporation in gaseous wells (10%), pressure changes (10%), temperature drops (5%) (4-6).

L.S.A. scales invariably emit alpha and beta particles and gamma rays (7); their presence in production plants can give rise to a gamma irradiation risk to the staff remaining for a long time in some particular plant areas and to a possible risk of internal radiocontamination to the staff involved in the scales or sludges mechanical removal and disposal.

That being stated a programme was started to determine uranium, thorium and radium in the scales, sludges and waters coming from Italy, Northern Sea and Africa.

Radioanalytical methods

The used radiochemical analysis was as follows. After the sample dissolution, ^{232}U and ^{228}Th were added as yield standards; the residue was dissolved in 2 M HNO_3 and the solution passed through a small column of Microthene (microporous polyethylene) 50-100 mesh supporting tri-octylphosphine oxide (TOPO); thorium was eluted with 1 M HCl and uranium with 1 M $(\text{NH}_4)_2\text{CO}_3$. After electroplating from $(\text{NH}_4)_2\text{SO}_4$, uranium and thorium alpha emitters were detected by alpha spectrometry. ^{226}Ra was determined by

counting Ba(Ra)SO₄ with a ZnS(Ag) detector after its separation from uranium and thorium and the decay of ²²⁴Ra (8). This technique was preferred to gamma spectrometry because of the presence of radioactive disequilibria in the ²³⁸U and ²³²Th families and taking into account the low activity to be measured.

Results and discussion

Taking into account the results shown in the tables I-III, the following conclusions can be drawn:

- 1) ²³⁸U and ²³²Th concentrations are either not detectable or very low ;
- 2) ²²⁶Ra concentration seems to be higher in oil extraction plants (800-3000 Bq/kg) than in other plants (30-400 Bq/kg), ²²⁶Ra concentration in the waters is very low because of its chemical behaviour;
- 3) for any specific plant, ²²⁶Ra concentration seems to be directly correlated to the extraction depth;
- 4) when uranium is detectable, the isotopes ²³⁸U and ²³⁴U are in secular radioactive equilibrium (Fig.1);
- 5) ²³²Th and ²²⁸Th are not always in equilibrium, especially in Tunisian scales, where the ratio ²²⁸Th/²³²Th can reach very high values, up to 700 (Fig.2). This fact can be due to the presence of initially high concentrations of the father ²³²Th from which ²²⁸Ra separated because of the different chemical behaviour of the two elements. Consequently the internal contamination risks could be caused not only by ²²⁶Ra, but also by ²²⁸Th and its daughters (²²⁴Ra, ²¹²Bi, ²²⁰Rn, ²¹⁶Po, ²¹²Po).

References

1. E & P Forum : "Low Specific Activity Scale origin, treatment and disposal", Report No 6.6/127, January 1988.
2. Mohammed Ibrahim El-Hattab : "Scale Deposition in Surface and Subsurface Production Equipment in the Gulf of Suez", Journal of Petroleum Technology, 1640-1652, September 1985.
3. O.J.Vetter : "Oilfield Scale - Can We Handle it?", Journal of Petroleum Technology, 1420-1408, December 1976.
4. J.Shen, C.C.Crosby : "Insight Into Strontium and Calcium Sulfate Scaling Mechanism in a Wet Producer", Journal of Petroleum Technology, 1249-1255, July 1983.
5. O.J.Vetter, R.C.Phillips : "Prediction of Deposition of Calcium Sulfate Scale Under Down-Hole Conditions", Journal of Petroleum Technology, 1299-1308, October 1970.
6. O.J.Vetter, V.Kandarpa, A.Harouaka : "Prediction of Scale Problems Due to Injection of Incompatible Waters", Journal of Petroleum Technology, 273-284, February 1982.
7. A.L.Smith : "Radioactive Scale Formation", Offshore Technology Conference, Houston, May 6-9, 1985.
8. C.Testa, D.Desideri, M.A.Meli, S.Bazzarri : "Separation and determination of uranium and radium-226 in phosphorites and their industrial derivatives by Extraction Chromatography", Journal of Radioanalytical and Nuclear Chemistry, 129/1, 191, 1989.

Tab.I: ^{238}U , ^{232}Th and ^{226}Ra concentration in different kinds of scale.

PLANT FEATURES	EXTRACTED HYDROCARBON	DEPTH (km)	CONCENTRATION (Bq/kg)		
			^{238}U	^{232}Th	^{226}Ra
EXTRACTION PLANT (PO VALLEY)	LIQUID	6	<0.9	<0.8	2890±578
EXTRACTION PLANT (PO VALLEY)	LIQUID	5	<0.9	<0.8	1126±225
EXTRACTION PLANT (PO VALLEY)	MIXED	5	<0.9	<0.8	120± 24
COLLECTION PLANT (PO VALLEY)	GASEOUS	-	23.8± 4.3	18.9±3.8	30± 6
COLLECTION PLANT (PO VALLEY)	GASEOUS	-	53.8±10.8	<0.8	<2.7
COLLECTION PLANT (SOUTHERN ITALY)	LIQUID	-	11.3± 2.3	<0.8	110± 22
OFF SHORE PLATFORM (NORTHERN SEA)	LIQUID	3	<0.9	<0.8	780±156
EXTRACTION PLANT (TUNISIA)	LIQUID	1	<0.9	<0.8	1323±265
TREATMENT PLANT (TUNISIA)	LIQUID	1	<0.9	<0.8	35± 7
PHASE SEPARATION PLANT (TUNISIA)	LIQUID	1	7.3±1.4	8.1±1.6	72± 15

Tab.II: ^{238}U , ^{232}Th and ^{226}Ra concentration in sludges.

PLANT FEATURES	EXTRACTED HYDROCARBON	DEPTH (km)	CONCENTRATION (Bq/kg)		
			^{238}U	^{232}Th	^{226}Ra
TREATMENT PLANT (TUNISIA)	LIQUID	1	4.6±0.9	13.0±2.6	69± 14
TREATMENT PLANT (TUNISIA)	LIQUID	1	10.3±2.1	33.0±6.6	175± 35
TREATMENT PLANT (TUNISIA)	LIQUID	1	6.7±1.3	2.6±0.5	393± 79

Tab.III: ^{238}U , ^{232}Th and ^{226}Ra concentration in waters.

PLANT FEATURES	EXTRACTED HYDROCARBON	DEPTH (km)	CONCENTRATION (Bq/kg)		
			^{238}U	^{232}Th	^{226}Ra
EXTRACTION PLANT (PO VALLEY)	MIXED	5	$<4.5\text{ E-}3$	$<4.0\text{ E-}3$	$20\text{ E-}1\pm4.0$
EXTRACTION PLANT (PO VALLEY)	LIQUID	2	$1.5\text{ E-}2\pm3.0\text{ E-}3$	$<4.0\text{ E-}3$	$2.3\text{ E-}1\pm4.6\text{ E-}2$
OFF SHORE PLATFORM (ADRIATICO SEA)	GASEOUS	1	$7.3\text{ E-}3\pm1.5\text{ E-}3$	$<4.0\text{ E-}3$	$6.0\text{ E-}2\pm1.2\text{ E-}2$

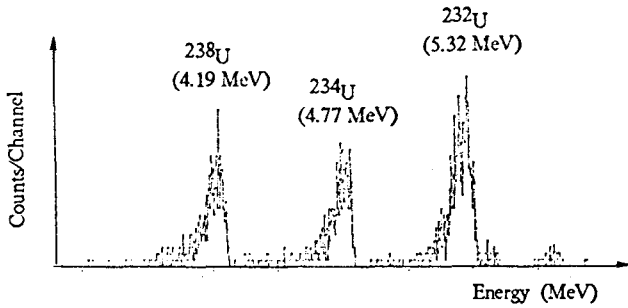


Fig.1:Uranium alpha spectrum

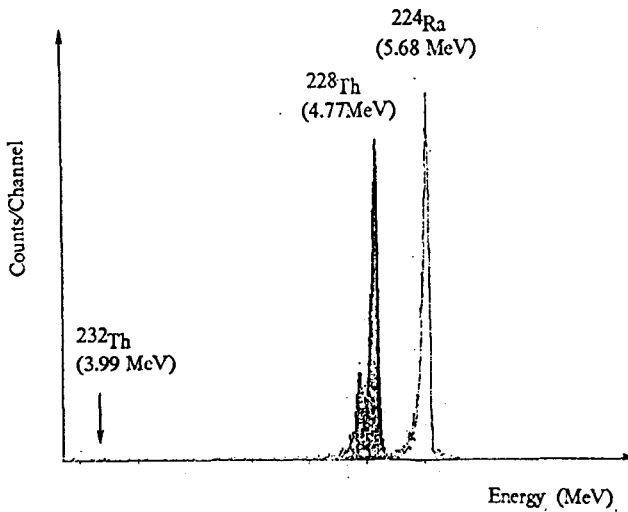


Fig.2:Thorium alpha spectrum