ENHANCED RADIOACTIVITY DUE TO NATURAL OIL AND GAS PRODUCTION

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INTRODUCTION

For more than 60 years it has been known that thermal brines can be enriched in natural radioactive substances. Such brines are raised to the surface together with natural oil and gas as an unwanted by-product. Already in 1927, A. Tcherepennikov (1) measured a radium concentration of $7.4 \cdot 10^{-10}$ % (250 Bq/l) in a brine sample taken from a well of the oil field Uchta in North East Russia. Since that time many papers on the geochemistry of radionuclides in oil and gas fields have been published mainly by Soviet scientists (2). First results for brines from German oil fields (near Hanover) were reported by H.J.Born (3) and ranged from less than 1 to 13 Bq/l. These brines consist mainly of sodium chloride, sometimes in saturated solution and with varying concentrations of alkaline earths. In gas fields excess salt from oversaturated brines is often precipitated after expansion, and scale is formed at the inner walls of tubings, pumps, separation and storage tanks. In many cases precipitates also result from the mixing of brines with surface waters (4). The equipment must then be exchanged from time to time for cleaning purposes.

Moreover, natural gas contains radon in various concentrations (5). Thus workers and consumers are likely to be exposed to enhanced natural radiation. Within the scope of a research contract (Federal Ministry of the Interior, St.Sch 872), a survey program was established for

- dose rate measurements at various production sites,
- assessment of the radionuclide content of brines and scales,
- assessment of the Rn-222 content in natural gas and
- aerosol measurements during cleaning work.

In this paper first results are presented and discussed.

INSTRUMENTS AND METHODS

Two scintillation dosimeters - H 7201 and PTB 7906 - have been used for dose rate measurements below and above 3 µSv/h.

Rn-222 was measured after transfer of the gas samples into 500 ml scintillation chambers (background count rate 0.5 min^{-1}, efficiency 68 %, detection limit 4 mBq/l at a counting time of 1000 min and a standard deviation of 10 %). Ra-226 in brines was measured according to the emanation method. Its decay product Rn-222 was emanated either directly from a brine sample or from the EDTA solution of the $BaSO_4$ precipitation into a 100 ml scintillation chamber (background counting rate 0.05 min^{-1}, Ra-226 efficiency 65 %, detection limit under the same conditions as above 1 mBq). The scintillation counter (BCIF China, type FD 125) was connected with an amplifier, discriminator, scaler and printer and calibrated with a PTB Ra-226 standard solution. A detailed description is given elsewhere (6). Scale samples were analysed for Ra-226, Ra-228, Th-228 and some other nuclides in a well-type Ge(Li) spectrometer.

Brines with higher activity concentrations were also measured with a Ge(Li) spectrometer using 400 ml Marinelli bakers. The results for Ra-226 measured according to the two methods agreed fairly well.

RESULTS

External Radiation

77 % of 83 surveyed well head sites did not show an increase in radiation above the natural background. Dose rates between 0.1 and 1 µSv/h were observed at 17 % of the sites investigated. At five sites, however, the dose rates were above 1 and up to 50 µSv/h. The highest dose rates were measured at the external surface of storage tanks for brines and were mainly caused by gamma radiation from Ra-226 contained in celestobaryte scales inside the tanks. In some cases slightly enhanced radiation observed on gas/oil separators was caused by Ra-222 and its daughter products contained in condensates. Under normal conditions the dose rates at working places were in all cases below the lower limit of a controlled area (7.5 µSv/h).

Radium Content of Brines

All brine samples analysed by gamma spectroscopy contained mainly Ra-226 and Ra-228. For 84 samples analysed for Ra-226 a variation range of more than 4 orders of magnitude was found. For 10 % of the samples the activity concentration was less than 4 mBq/l but another 10 % exceeded 20 Bq/l. The median value was 1.5 Bq/l. Ra-226 concentrations of 80 Bq/l were found in brine samples from several gas fields close to the Dutch border.

Specific Activity of Scales

Ra-226 and Ra-228 are also the dominating radionuclides in scales and other precipitates. In addition, Th-228 (depending on the age of the precipitate) and sometimes significant amounts of Pb-210 (in samples from East Hanover gas fields) were found. Specific activities up to 1 kBq/g were found for samples of $BaSO_4$ scale. The specific activity of $CaCO_3$ scales is usually much lower but such scales may contain Ac-227 as the dominating radionuclide. The activity ratio Ra-228/Ra-226 was found to be higher than 1 in samples from oil fields and lower than 1 in most of the samples from gas fields (variation range 0.056 to 4.4). Some results of gamma spectrometric analyses are presented in Table 1.

Table 1:

Specific activities in Bq/g of some scales and other precipitates

Nuclide	Sample No.					
	114/10426	126/10983	33/11070	33/10972	190/BP1	190/BP2
Ra-226	59	350	160	7.4	1000	0.85
Pb-210	-	-	30	70	22	1.4
Ac-227	n.d.	n.d.	n.d.	n.d.	n.d.	2.5
Ra-228	240	7.4	120	5.9	<10	n.d.
Th-228	48	n.d.	26	1.6	<10	n.d.
$\frac{\text{Ra-228}}{\text{Ra-226}}$	4.1	0.02	0.75	0.8	< 0.01	-

n.d. = not detectable
- = not analysed

Sample description:

No.	Origin	physical form	chemical form
114/10426	oil field	scale	$Ba/SrSO_4$, PbS
126/10983	gas field	scale	$Ba/SrSO_4$
33/11070	gas field	scale	Pb, $Ba/SrSO_4$
33/10972	gas field	deposition	SiO_2, PbS, Hg
190/BP1	gas field	scale	-
190/BP2	gas field	scale	$CaCO_3$

Rn-222 Content of Natural Gas

140 gas samples mainly from North German gas and oil fields were measured until summer 1983. The radon concentrations are log-normally distributed and range from less than 0.1 Bq/l (15 % of the samples) up to 4 Bq/l with a median value of 0.30 Bq/l. 15 % of the samples exceed 1 Bq/l. Values in the upper range were found in gas samples from Permian deposits near the Dutch border and from lower new red sand-stone deposits in the Ems-Weser area. In general a relationship between radon and other gas constituents could not be ascertained. 30 samples from the Emsland gas field, however, showed a weak positive correlation ($r^2 = 0.45$) between Rn-222 and n-butane.

In most cases the gas samples were taken near the well heads. The average Rn-222 concentration in gas samples taken during half a year from the distribution line in Brunswick was only 0.11 Bq/l (variation range from 0.06 to 0.15 Bq/l).

DISCUSSION AND CONCLUSIONS

It is shown that radioactive scales in tubings, pumps and storage tanks can be detected with common radiation protection dosimeters. Under normal conditions of operation the annual dose for workers due to external radiation from such sources will not, however, exceed 5 mSv.

According to Article 4, of the Euratom Directive (7), notification and prior approval are not required for radioactive materials with a specific activity of less than 100 Bq/g. For solid natural radioactive materials this exemption limit is even increased to 500 Bq/g. About 20 % of the investigated scale and precipitate samples exceeded

this value. It was common practice to remove the scale from the inner walls of the gas tubes by sand-blasting until results of aerosol measurements were submitted (PTB Report 6.62-862/1, not for publication): The derived activity concentrations (DAC) according to ICRP 30 (8) may be exceeded by one order of magnitude, even if the specific activity of the scale to be removed is less than the exemption limit of 500 Bq/g.

In the Federal Republic of Germany, the exemption limits mentioned above are not applicable to waste disposal. According to a very restrictive legal requirement, waste containing highly toxic radionuclides must be considered as radioactive if the specific activity exceeds 0.37 Bq/g, and normal disposal of such waste requires prior approval. As a way out of this legal problem, scales and other precipitates from oil and gas production may be considered as by-product materials which could be used, for instance, together with concrete to refill old wells.

Up to now the large quantities of brines which are raised to the surface together with oil and gas have not raised any problems. These brines are re-used for the extraction of oil from its deposits.

Sewage sludge from oil processing plants is used in agriculture as a soil improver. This is permitted without any limitation of the specific activity as far as radionuclides of natural origin are concerned. For other nuclides the limit is as low as 0.37 Bq/g.

The radiation exposure of the population due to natural gas consumption is negligible, taking into account a median Rn-222 concentration of 0.3 Bq/l at the well (which is just 10 times higher than the radon concentration in dwellings due to the exhalation from building materials) and an even lower concentration due to its short half-life when it is consumed. It should, however, be noted that Rn-222 concentrations of 700 Bq/kg have been measured in certain liquid gas condensates which require further investigations.

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