GAS GENERATION MEASUREMENTS IN DRUMS CONTAINING LL/ILW

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ABSTRACT

To obtain reliable estimates of the quantities and rates of production of gases measurements were carried out in drums containing LL/ILW. Repeated sampling of 10 drums was possible using a specially designed outlet. Qualitative and quantitative analysis of headspace gases were performed during a two year period. The composition of these gases depended on the type of the waste and its conditioning. The drums were non hermetic so the internal pressure was not higher than 1,2 bar in any of them. In most of the drums the headspace was depleted in oxygen. Significant increase of hydrogen was found only in some of these drums. Organic compounds appeared in the drums filled with compacted solid waste. The stable isotope measurement ($\delta^{13}C$, $\delta^{18}O$) combined with ^{3}H and ^{14}C measurement of water vapours, CH_4 and CO_2 explain the possible sources of CO_2 and CH_4 generation.

INTRODUCTION

The FEP list of every safety assessment has to consider the gas formation during the storage of radioactive waste. Understanding the governing mechanisms is an important step in the prediction of cumulative volumes of gas generated within the repository and of the variation of the rate of gas generation with time.

Studies indicated that in low and medium level radioactive wastes substantial quantities of gas would be produced in reactions involving certain components of the waste forms and their containers.

The main accountable processes for gas generation are principally the metal corrosion producing hydrogen [1-5] and microbial degradation of organic particularly cellulose wastes [6-10]. Hydrogen sulfide may also form in significant quantities from microbial action of sulfate ions [11-15]. It is likely that a small proportion of the generated gases will be radioactive as a result of the incorporation of the isotopes ^{3}H and ^{14}C that are present within the waste [16-17]. A third process, radiolysis was found to have the potential to generate relatively small volumes of gas compared to corrosion and microbiological degradation.

In the present study gas composition measurements have been carried out on samples taken from the headspace of 10 drums containing LL/ILW generated and temporarily stored at Paks NPP.

SAMPLING AND MEASUREMENTS

The solid (or solidified) low level or intermediate level radioactive wastes temporarily stored at the site of Paks NPP are packed into 200 l stainless steel drums. The compacted wastes consist of

contaminated trash and scrap, protective clothes, gloves, towels, mainly plastics, textile, wood and paper.

The non-compacted wastes consist of debris of building material, out-of-use tools, mainly metals. The grouted sludge comes from cleaning (steam generators, floor in labs and workshops, etc.) and does not contain used ion exchange resin or evaporator concentrate.

The drums have been equipped with a special gas outlet system [18] to make repeated sampling possible (the parameters of the investigated 10 drums are given in Table. 1.)

The qualitative and quantitative analysis of headspace gases were made as follows:

- the in situ qualitative determination of different components of gases was made using a quadrupole mass spectrometer (OMNISTAR, Balzers)
- 1 litre gas sample was taken in stainless steel flask from each drum and transported to the lab for further investigations. The laboratory analysis consisted in C and O stable isotope measurements (MS), radiocarbon and tritium activity determination (GPC and LSC) and He isotope ratio measurements (VG-5400, noble gas MS).

RESULTS

Qualitative Analysis

The parameters of the investigated 10 drums together with the results of qualitative analysis are given in Table 1.

Table I Parameters of the Investigated Drums

Drum code	Type of waste	Max. dose rate (nGy/h)	Date of closing	Main components of bulk gas	Pressure of bulk gas (bar)
1T	compacted	1200	25/03/98	**N_2, O_2, Ar, CO_2**	1.00
2T	compacted	4200	23/03/98	H_2, **N_2**, O_2, **Ar**, **CO_2**	1.10
3T	compacted	2800	24/03/98	**H_2**, **N_2**, O_2, Ar, **CO_2**, CH_4	1.04
4T	compacted	2500	19/03/98	**H_2**, **N_2**, O_2, **Ar**, CO_2	1.02
1NT	non compacted	1200	03/04/98	**N_2, O_2, Ar, CO_2**	1.00
2NT	non compacted	4500	29/04/98	**H_2**, **N_2**, O_2, **Ar**, **CO_2**	1.07
3NT	non compacted	2000	24/04/98	**N_2, O_2, Ar,** CO_2	1.00
1S	grouted sludge	2000	10/05/99	**CH_4**, **N_2,** O_2, Ar**, CO_2**	1.26
2S	grouted sludge	1800	06/05/99	**CH_4**, **N_2,** O_2, Ar**,** CO_2	1.08
3S	grouted sludge	2500	08/10/99	**N_2, O_2, Ar,** CO_2	1.00

Gases with higher concentration than 1% are written in bold. The measured pressure values in the drums and the pressure testing of an empty drum also proved that these drums are not hermetically closed.

Quantitative Analysis

The quantitative analysis of the gases was performed in the laboratory and the results are presented below:

- Composition of the headspace gases was extremely different even in the case of drums containing similar type of waste.
- Hydrogen formation could be detected in four drums: 2T, 3T, 4T and 2NT. The H_2 concentration in the bulk gas was about two times more at the end of the measured period than at the beginning. In drum 2T only a small amount of hydrogen was detected but the increase of the concentration was also observable. The maximal H_2 content was less than 10 %.
- Each drum contains nitrogen because they were closed under atmosphere. Dramatic nitrogen decrease was detected in two drums, which contain grouted sludge waste (1S, 2S). The main reason of this variation is the high rate methane formation. The large amount of the produced gas replaces the nitrogen (and the other air origin gas components) from the drum. The bulk gas of drums filled with compacted waste (1-4T) contains almost only nitrogen (≈ 100 %). That might be the effect of oxygen consumption due to microbial activity.
- Each bulk gas contains more or less CO_2 surplus related to the composition of air. This gas is the product of many degradation processes. The highest CO_2 concentration was found in the drum 1S (40%).
- At the time of closing each drum contains a high amount of oxygen because they were closed under atmosphere. The initial 20 % O_2 concentration only in two drums (3NT, 3S) remained constant during the whole measured period. In drum 1NT significant oxygen decrease was detected. The oxygen content of the other drums was very low or undetectable.
- Powerful methane formation was detected in drums 1S and 2S. At the beginning of measured period the methane content of bulk gas of 2S was far lower than in drum 1S (≈ 80 %!) but due to high formation rate during the last period of storage the concentration in the drum reached 70 %.

Stable Isotope Ratio Measurements

In order to determine the origin of CO_2 surplus in the headspace gases, stable isotope measurements were made. The carbon and oxygen stable isotope ratios are presented in Table II:

Table II. $\delta^{13}C$ Values Measured in the Headspace Gases

Drum code	CO_2 fraction		CH_4 fraction	
	average cc. (%)	$\delta^{13}C$ (‰) (PDB)	average cc. (%)	$\delta^{13}C$ (‰) (PDB)
1T	6.3	-20.4	-	
2T	3.9	~ 112*	-	
3T	3.3	-22.9	0.1	-23.7
4T	0.8	-*	-	
1NT	13.2	-26.7	-	
2NT	17.5	-25.8	-	
3NT	0.2	-22.4	-	
1S	37.8	0.5	59.8	-48.4
2S	5.7	-9.6	31.9	-38.3
3S	0.4	-31.3	-	

*the separation and gas cleaning procedure failed

The results are referred to the PDB standard (Belemnite from the Peedee Formation in South Carolina), which had by definition $\delta^{13}C$ of 0 ‰.

The fraction in the drums containing compacted and non compacted wastes were in the range –20 to –30 ‰. These values are more negative than for the atmospheric CO_2 ($\delta^{13}C \approx -10$ ‰), which prove the organic nature of CO_2 gas generation in the drums. The organic origin of carbon dioxide is probably a consequence of the decomposition of single-use gloves, paper, plastics and rubbers etc.

The drums containing grouted sludge (in which the methane formation is significant) present high negative delta carbon thirteen values for CH_4 and slightly negative or positive delta carbon thirteen values for CO_2. These results can be explained only with considerable bacterial processes taking place into the drums.

Radiocarbon and Tritium Activity Concentration of the Headspace Gases

The tritium and radiocarbon measurements data obtained for the drums in study are presented graphically in Fig. 1:

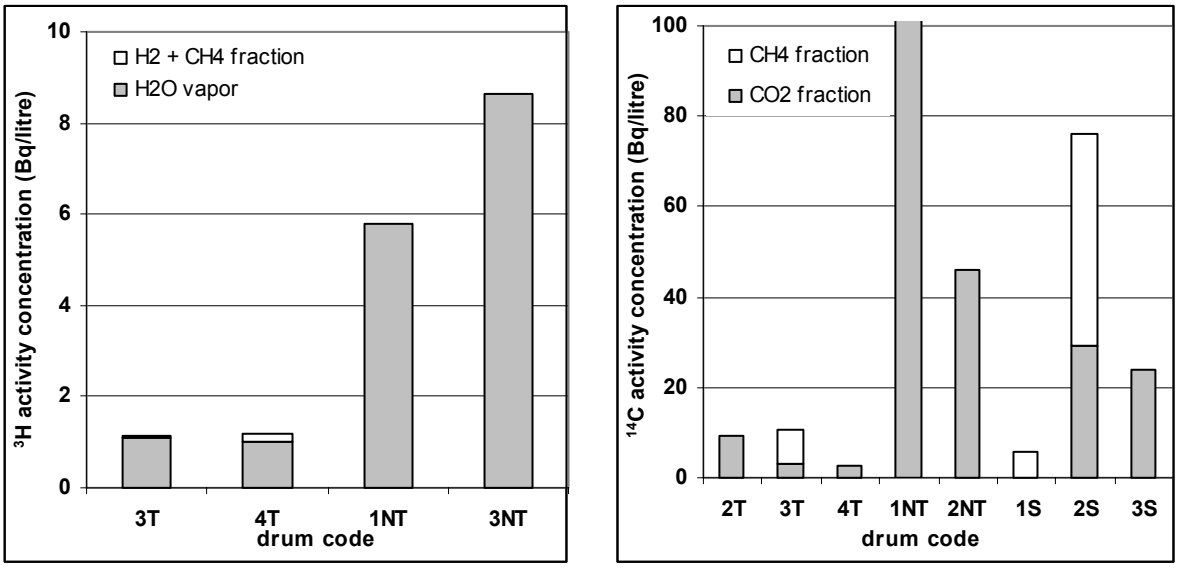

Fig.1. Tritium activity concentration and radiocarbon activity concentration in the drums containing LL/ILW.

The figures show only the drums in which the tritium or radiocarbon activity concentration was higher than 1 Bq/l.

Tritium was measured in the water vapor and H_2+CH_4 fraction, while radiocarbon was measured in the CO_2 and CH_4 fraction, respectively.

Relatively high and constant tritium activities were measured in the bulk gases of drum 3T, 4T, 1NT, and 3NT. The bulk gases of drums 1T, 2T contained tritium about 0.1 Bq/litre.

Considerable amounts of radiocarbon were measured solely in the drums closed earlier, but these values are relatively constant compared to the tritium data of individual drums.

CONCLUSIONS

- The gas formation processes vary from one drum to the other.
- Quantitatively it can be stated that in general during the storage period the carbon dioxide content increased and oxygen content decreased.
- Hydrogen production was detected mainly in drums containing compacted wastes. The maximal value measured was less than 10 %, while oxygen was depleted in these drums.
- In two drums the rate of the gas generation was extremely high. In these cases methane and carbon dioxide were generated in rather high amount, and the oxygen was used up.
- Carbon dioxide generation is characteristic for all types of drums, while methane formation is typical for drums containing grouted sludge.

- The stable isotope ratio measurements proved that the surplus of CO_2 measured in almost all drums is of organic origin.

- Significant variation in time of tritium in the individual drums was observed. The maximal measured value was approx. 80 Bq/litre, but values about 10 Bq/litre were also detected. The typical tritium activity concentration values were between 0.1 and 10 Bq/litre.

- The highest radiocarbon activity concentration measured in the headspace gases was about 3000 Bq/litre. Typical ^{14}C activity values were between 1 and 100 Bq/litre.

- The presented results represent only the first stage of a long-run investigation. Continuous sampling of these drums can help us to understand gas-formation processes in different type of LL/ILW. Further studies will focus on calculation of gas generation rates using the presented measurement data.

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