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COMPOSITION AND ACTIVITY VARIATIONS IN BULK GAS OF DRUM WASTE PACKAGES OF PAKS NPP

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ABSTRACT

To obtain reliable estimates of the quantities and rates of the gas production a series of measurements was carried out in drum waste packages generated and temporarily stored at the site of Paks Nuclear Power Plant (Paks NPP). Ten drum waste packages were equipped with sampling valves for repeated sampling. Nine times between 04/02/2000 and 19/07/2001 qualitative gas component analyses of bulk gases of drums were executed. Gas samples were delivered to the laboratory of the ATOMKI for tritium and radiocarbon content measurements.

1 INTRODUCTION

During the storage of low and intermediate level radioactive waste (L/ILW) generated in Paks Nuclear Power Plant (Paks NPP) significant quantities of gas may be produced. These wastes are packed into containers of steel (drums). The operational L/ILW contains only very small amounts of long-lived radionuclides. It needs to be disposed in a repository, although it will decay to harmless levels in a relatively short time.

The available data of individual waste drums of Paks NPP are: dose rate at the surface and classification of the stored waste. These classifications are: *sludge waste* comes from cleaning (steam generators, floor in labs and workshops, etc.), *non-compacted waste* consist of debris of building material, out-of-use tools, mainly metals and *compacted waste* contains contaminated trash and scrap, protective clothes, gloves, towels, mainly plastics, textile, wood and paper.

The main accountable processes for gas generation are principally the metal corrosion and microbial degradation of organic, particularly cellulosic wastes. It is likely that a small proportion of the generated gas will be radioactive as a result of the incorporation of the isotopes ^{3}H and ^{14}C that are present within the waste.

In order to asses the implications of gas generation for the safety of a repository of L/ILW, it is important to gain an understanding of the principal mechanisms of gas generation and estimate the rate of gas formation and the possible radioactivity of generated gases

Preliminary estimates indicated that in L/ILW substantial quantities of gas would be produced in reactions involving certain components of the waste forms and their containers. It was concluded that gases, which could be mainly produced, are: hydrogen (by corrosion of metals), methane and carbon dioxide (by microbial activities) (Greenfield et al., 1990; Watkiss et al., 1993; Biddle et al., 1987; Rees et al, 1988; Rees, 1989; Agg et al., 1993). Because of the relatively low radionuclide content the contribution of radiolysis to the gas generation is not significant. Radioactive gases had to be considered are mainly the gases noted above, in which atoms of hydrogen and carbon are replaced by the β-emitters tritium (^{3}H) and radiocarbon (^{14}C), respectively (Yim et al., 1996; Jefferies, 1990).

In spite of the wide-range experimental investigations concerning the gas generation (Nirex, Pacific Northwest Laboratory, Westinghouse Hanford Company, Argonne National Laboratory), the available data measured in real L/ILW drums are very limited (Eder & Lierse, 1995). To obtain reliable estimates of the quantities and rates of the production of gases a series of measurements was carried out in drum waste packages generated and temporarily stored at the site of Paks NPP.

2 EXPERIMENT

Ten drum waste packages, temporarily stored at the site of Paks NPP, were equipped with sampling valves for repeated sampling by a researcher team of the Institute of Nuclear Research of the Hungarian Academy of Sciences (ATOMKI) Each of them was equipped with sampling valve on 04/02/2000. These packages were closed at different dates in the previous two years, before closing they were opened in the atmosphere. During the setting procedure mixing of external air and the internal bulk gas was precluded by appropriate design of sampling valves and the setting method (Molnár et al., 2000).

Using a special sampling system designed in the ATOMKI the mass spectrums of bulk gases of drums were measured (Molnár et al., 2000) directly after the valve-setting. The results of spectrum analyses show considerably different bulk gas compositions developed since drums were closed. The parameter of investigated drums and the main components of their bulk gases are presented in Table 1. 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 this type of drums is not hermetically closed for gases. At the closing edges the gas can come out from the drum.

Nine times between 04/02/2000 and 19/07/2001 qualitative gas component analyses were executed by a properly calibrated quadruple mass spectrometer (Omnistar, Balzers) on the spot, at the site of the Paks NPP. Several times gas samples from the bulk gas were collected from each drum into glass bulbs and these samples were delivered to the laboratory of the ATOMKI for further isotope measurements.

Code of drum	Type of waste	Max. dose rate (nGy/h)	Date of closing	Main components of bulk gas on 04/02/2000	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**	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

Table 1. Parameters of the investigated drums

2.1. Sample preparation

In the first step different gas components were separated from each other by cryogenic gas separation methods. The schematic drawing of the gas separator and burning system built in the ATOMKI is presented in Figure 1.

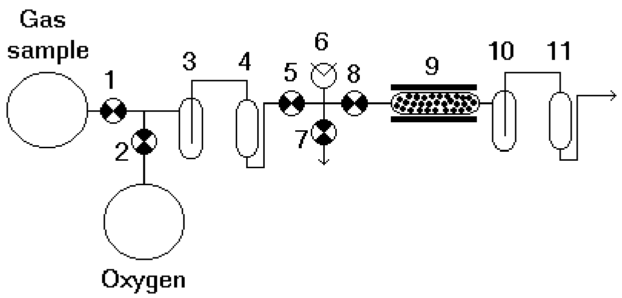

Figure 1.: Gas separator and burning system developed in the ATOMKI

In case of gas samples not containing hydrogen or methane only the first part of the system was used without the oxygen bulb. In this case the sample preparation means water vapour and carbon dioxide collection from the sample. During this process the valves 5. and 7. are opened and the dart in the figure shows the direction of continuous vacuum pumping. The vapour trap (3) is cooled at the temperature of 208 K by cold isopropyl alcohol to froze the water from the gas. The carbon dioxide trap (4) is cooled at the temperature of liquid nitrogen (77 K). At this temperature the total CO_2 content of the gas is frozen to the inner surface of the glass trap. The CO_2 trap has own valves, which are closed at the end of the gas collection so the collected gas cannot escape from it. A pirani vacuum controller (6) helps us to stabilize the pressure about 10-15 mbar in the system with opening valve 1. In this range of pressure the efficiency of the gas collection by above mentioned freezing methods has about 100%.

Valve 8. is only opened if the gas sample contains burnable hydrogen or methane. During the separation process hydrogen or methane was burned in kiln (9) at the temperature of 673 K. The kiln is filled with catalysator material (Pt-Pd 2-2% on Al_2O_3 pellets, BASF), which helps the burning. A separate oxygen bulb is also opened (valve 2) for ensuring enough oxygen for burning. The burned hydrogen in water vapour form (in trap 10.), the burned methane in water vapour (in trap 10.) and carbon dioxide form (in trap 11.) are collected in the same way than in the first part of the system.

2.2. Tritium measurements

The vapour samples were washed out from the traps by tritium free distilled water until the final volume of a sample reaches the 5ml value. This sample was mixed with 15 mL Ultima Gold LLT (Packard) scintillator cocktail in a 20 mL vial. The tritium content of the sample was measured by a calibrated low background liquid scintillation counter (TRICARB 3170TR/SL).

2.3. ^{14}C measurements

A certain part of the collected CO_2 gas was mixed with a relatively large amount of inactive high purity CO_2 gas. This diluted, high volume sample was suitable for measuring by a calibrated low background gas proportional counter (GPC), developed in the ATOMKI. This measurement requires at least 1 litre volume of CO_2 sample and the maximal allowed activity for this counter is about 1 Bq per sample. These were the reasons why only small parts of collected CO_2 samples were diluted with inactive gas.

3 RESULTS

Composition of the headspace gases was extremely different from each other even in the case of drums containing similar type of waste. During the nine occasions of composition measurements of headspace gases in the period between 04/02/2000 and 19/07/2001 very different processions were detected in the individual drums.

3.1. Hydrogen content variation

Hydrogen formation could be detected in four drums: 2T, 3T, 4T and 2NT.

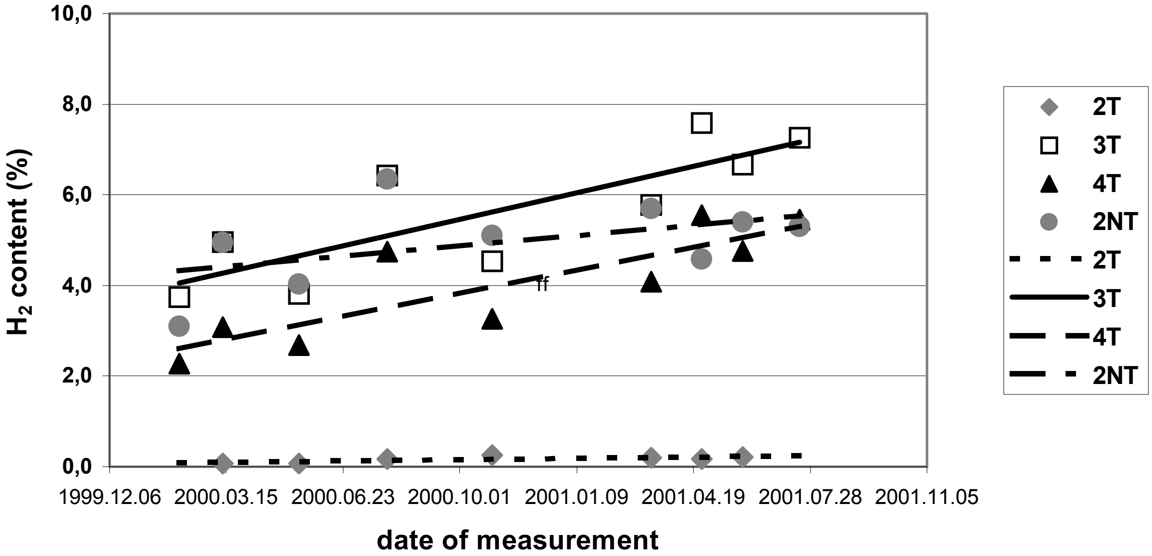

Figure 2: H_2 content variation of the headspace gas in drum L/ILW packages

In drums 3T, 4T and 2NT significant increasing of hydrogen content was detected.

The H_2 concentration in the bulk gas was about two times more at the end of the measured period than at the beginning. The continuous increasing is presented in Figure 2. In drum 2T only a small amount of hydrogen were detected but the increasing of the concentration is also observable.

3.2. Nitrogen content variations

Each drum contains nitrogen because they were closed in the atmosphere. Dramatic nitrogen content decreasing was detected in two drums, which contains grouted sludge waste (1S, 2S) (Figure 3.). The main reason of this variation is the high rate methane formation. The large amount of the produced gas is continuously extruding the nitrogen (and the other air-origin gas components) from the certain drum. The bulk gas of drums filled with compacted waste (1-4T) contains almost only nitrogen. That might be the effect of oxygen vanishing due to microbial activity.

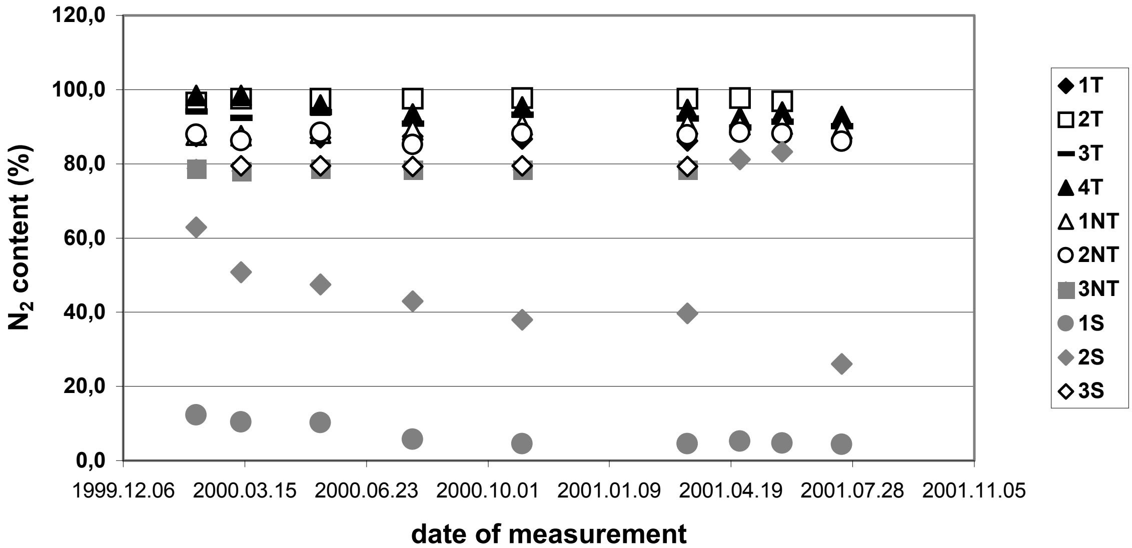

Figure 3.: Variation of nitrogen concentration of bulk gases in drum L/ILW packages

3.3. Methane content variations

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 (it is about 80%!), but due to the rather high formation rate during the last year the concentration of it neared the 70% in that drum too.

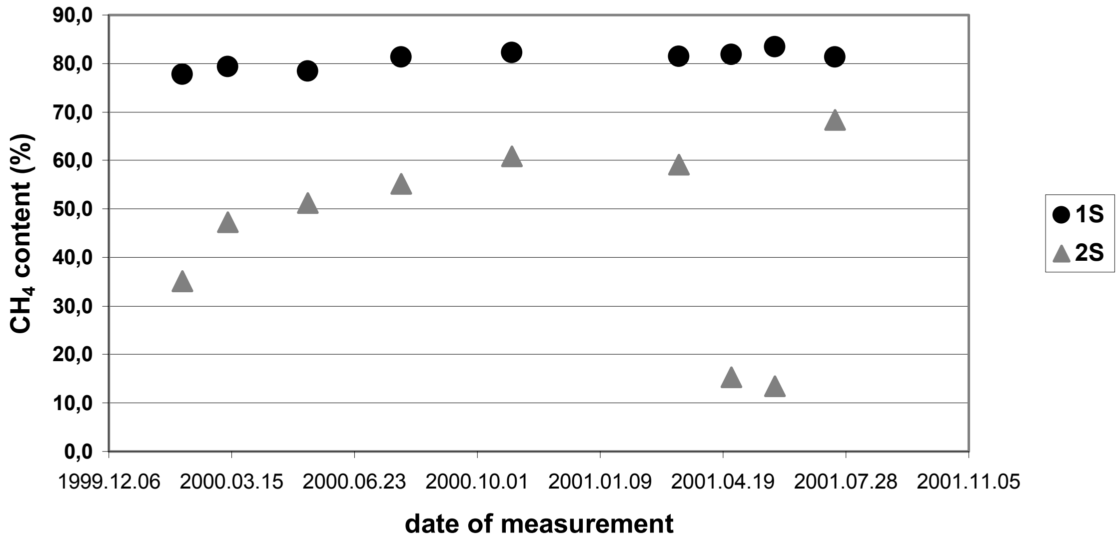

Figure 4.: Variation of methane concentration of bulk gases in drum L/ILW packages

3.4. Oxygen content variation

At the time of closing each drum contains a high amount of oxygen because they were closed in the atmosphere. The initial 20% O_2 concentration only in two drums (3NT, 3S) remained constant during the whole measured period

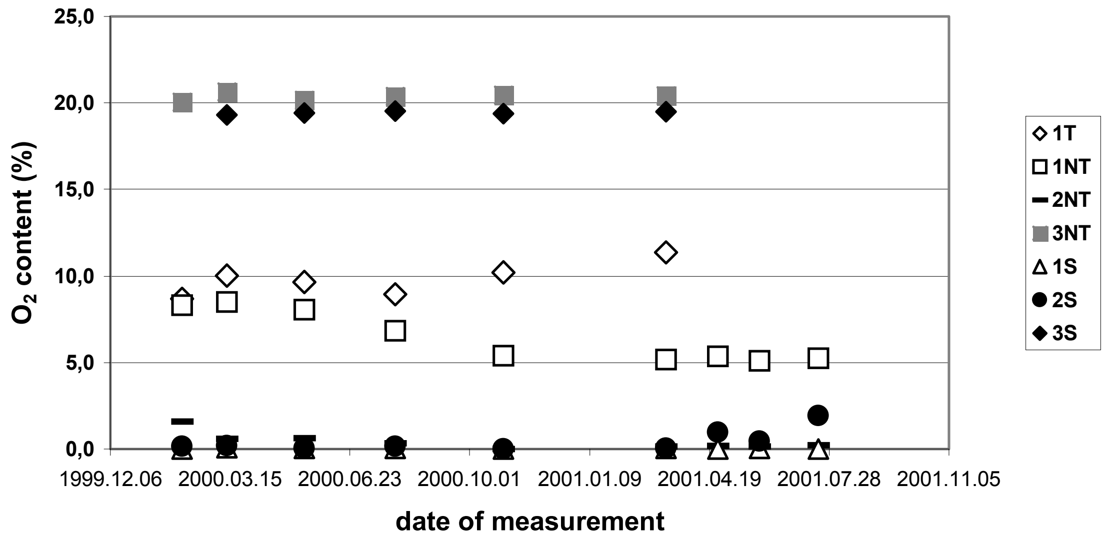

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Figure 5.: O_2 content variation of the headspace gas in L/ILW drum packages

In drum 1T the half of the original concentration seems to be constant. In drum 1NT significant oxygen content decreasing was detected. The oxygen content of the other six drums is very low or undetectable.

3.5. Carbon dioxide content variation

Each bulk gas contains more or less CO_2 surplus related to the composition of air (Figure 7.). This gas is the product of many degradation processes. The highest CO_2 concentration was found in the drum 1S.

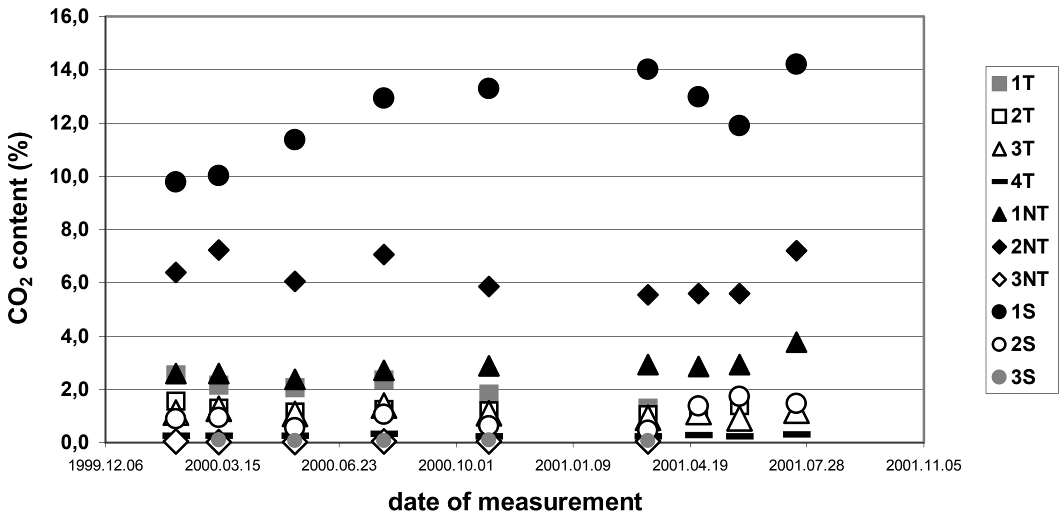

Figure 6.: CO_2 content variation of the headspace gas in drum L/ILW packages

3.7. Tritium content

The presented data in Figure 7. are the summarized tritium activities concentrations came from water, methane and hydrogen content of individual drums.

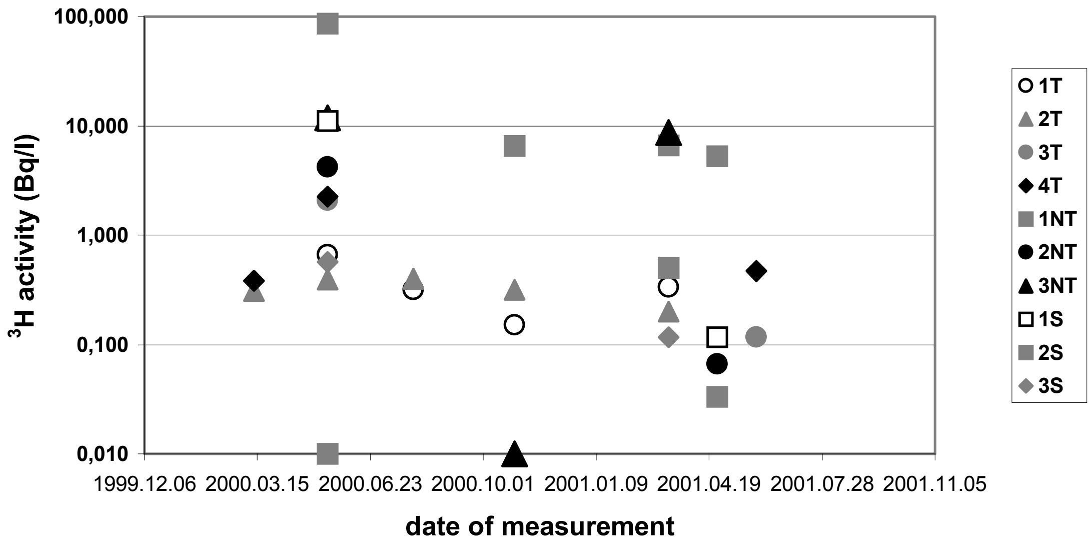

Figure 7.: The total ^{3}H activity concentration of the headspace gas in drum L/ILW packages

Tritium activity values show high diversity. Significant tritium activity decreasing was detected in drums in which relatively high rate of gas production was indicated. (drum 1S, 2S, 2NT and 3T). Relatively high and constant tritium activities were measured in the bulk gases of drum 4T, 1NT, and 3NT. Lower and constant tritium activities were measured in the bulk gases of drum 1T, 2T.

3.8. Radiocarbon content variations

There are also high varieties between the total ^{14}C activity concentration values of different drums, but these values are relatively constant compared to the tritium data of individual drums.(Figure 8.).

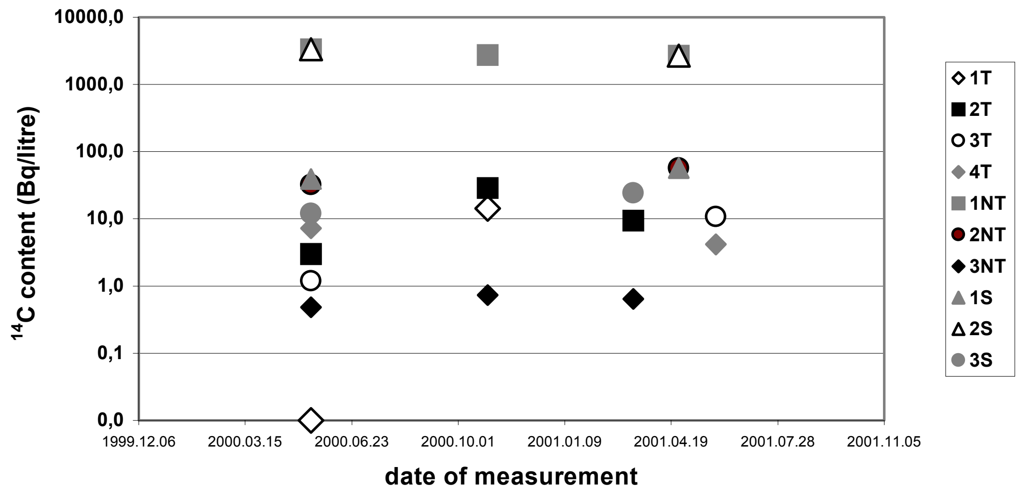

Figure 8.: The total ^{14}C activity concentration of the headspace gas in drum L/ILW packages

4 CONCLUSIONS

The gas formation processes in the individual drums were very different. Generally the carbon dioxide content increased and oxygen content decreased. Hydrogen production were detected in four drums, the maximal value was less than 10%. Oxygen was depleted from 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.

No relationship was found between the total activity of the waste stored in the drums and the amount and rate of the gas generation. It seems to be likely that the gas formation is controlled by corrosion and/or bacterial activity and the radiolysis plays a minor role.

Tritium activity concentration values show high diversity. Significant variation of tritium content in individual drums with time was also typical. The maximal value was more than 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. Often the values shows decreasing tendency.

Also high differences were measured in radiocarbon content of the different drums, but these values represent smaller diversity with time in case of the individual drums than tritium contents. Maximal measured radiocarbon activity concentration from the bulk gas of drum L/ILW packages was about 3000 Bq/litre. Typical ^{14}C activity values were between 1 and 100 Bq/litre.

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