International Conference
Nuclear Energy in Central Europe 2000
Golf Hotel, Bled, Slovenia, September 11-14, 2000
sponsored

GAS FORMATION IN DRUM WASTE PACKAGES OF PAKS NPP

Mihaly Molnár, László Palcsu, Éva Svingor, Zsuzsa Szántó, István Futó
Institute of Nuclear Research of the Hungarian Academy of Sciences
4001 Debrecen P.O.Box: 51., Hungary
mmol@moon.atomki.hu

Peter Ormai
Public Agency for Radioactive Waste Management (PURAM)
H-2040 Budaörs, Puskás Tivadar str. 11, Hungary

ABSTRACT

Gas composition measurements have been carried out by mass spectrometry analysis of samples taken from the headspace of ten drum waste packages generated and temporarily stored at Paks NPP. Four drums contained compacted solid waste, three drums were filled with grouted (solidified) sludge and three drums contained solid waste without compaction. The drums have been equipped with a special gas outlet system to make repeated sampling possible. Based on the first measurements significant differences in the gas composition and the rate of gas generation among the drums were found.

1 INTRODUCTION

Low and intermediate level radioactive waste (L/ILW) generated in Paks NPP containing mainly spent ion exchange resins used for water purification, contaminated trash and scrap, protective clothes, gloves, towel are packed into containers of steel (drums), in some cases first solidified (conditioned). The L/ILW operational waste 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.

During the storage significant quantities of gas may be generated within the drums, principally by the coupled processes of metal corrosion and microbial degradation of organic, particularly cellulosic wastes. It is likely that a small proportion of the generated gas will be radioactive, principally as a result of the incorporation of the isotopes ^{3}H and ^{14}C that are present within the waste.

If gas were to be contained within the repository, a build-up of pressure would occur. This could have an effect on the engineered structure and host rock, and lead to a disturbance of the pressure-head gradients and groundwater flows in the vicinity of the repository. On the other hand, if gas were to escape from the repository into the geosphere, various possible consequences should be considered. Within the geosphere, the gas might have an effect on the local groundwater flow regime. Within the biosphere, there are potential hazards associated with the release of radioactive and flammable gases.

In order to assess the implications of gas generation for the safety of a repository for L/ILW, it is important to gain an understanding of the principal mechanisms of gas formation. This understanding can then be used to assist in the prediction of the likely cumulative volumes of gas generated within the repository, and of the variation of the rate of gas generation with time.

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 in the site of Paks NPP.

2 GENERATION OF BULK GASES IN L/ILW DRUM WASTE PACKAGES

Preliminary estimates 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. It was concluded that there were two main sources of gas (Greenfield et al., 1990; Watkiss et al., 1993; Biddle et al., 1987; Rees et al, 1988; Rees, 1989; Agg et al., 1993):

(a) hydrogen generated by the corrosion of metals (Marsh, 1988; Sharland & Newton, 1989; Naish et al., 1993; Sorensen et al., 1990; Simpson & Weber, 1988);

(b) methane and carbon dioxide, produced in approximately equal amounts by microbial degradation of cellulosic materials, mainly wood and paper. Hydrogen sulphide may also form in significant quantities from microbial action on sulphate ions in wastes (Agg, 1993; Agg et al., 1995; Chan et al., 1996; Agg et al., 1997; Barlaz et al., 1987; Yim et al., 1996; Halvadakis, 1983; Humphreys et al., 1997; Hoeck, 1983).

A third process, radiolysis, was found to have the potential to generate relatively small volumes of gas compared to corrosion and microbiological degradation.

Two other types of gas could also form, but only in small amounts:

(a) radioactive gases, particularly of the bulk gases noted above, in which atoms of hydrogen and carbon are replaced by the β-emitters tritium (^{3}H) and carbon-14 (^{14}C) respectively (Yim et al., 1996; Jefferies, 1990);

(b) other toxic, inactive gases formed mainly in microbial processes.

(a) Formation of hydrogen by anaerobic corrosion

The drums contain significant quantities of metallic materials. These include the containers and some components of the waste. The first category consists of mainly stainless and carbon steels; the second includes stainless and carbon steel from tools, and smaller amounts of other potentially reactive metals such as aluminium and brass. The various metals in contact with water present in the drum undergo corrosion reactions with the formation of gases, mainly hydrogen.

Steel can be considered to corrode by two different mechanisms. Immediately after closure of the drum, while there is oxygen available, an aerobic mechanism that will not lead to the formation of any gas will apply:

$$4Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_3$$

This mechanism will last as long as there is available oxygen in the drum. When all the oxygen is used up, a reducing environment will be established and the anaerobic corrosion mechanism will take over with the production of hydrogen gas:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2.$$

(b) Production of carbon dioxide and methane by microbial action

It is well established that certain organic materials can undergo microbial decomposition under both aerobic and anaerobic conditions to produce gaseous products, predominantly carbon dioxide and methane. Studies of the disposal of domestic waste in landfill sites have indicated that the microbial generation of these major gaseous components follows a characteristic sequence. There is an initial period of aerobic respiration where oxygen trapped during deposition of the wastes is rapidly utilized by bacteria generating carbon dioxide. Anaerobic microbial activity begins in the second phase and is mainly controlled by the hydrolysis of organic materials to produce intermediate compounds, such as carboxylic acids, together with the gaseous products, mainly carbon dioxide and some hydrogen. Finally methanogenic bacteria utilize carbon dioxide, hydrogen and acetic acid to produce methane. During this stage the action of sulfate-reducing bacteria on sulfate ions present within the waste may produce hydrogen sulfide in preference to methane. In a similar way, nitrate-reducing bacteria can participate in the formation of nitrogen gas.

3 SAMPLING AND MEASUREMENTS

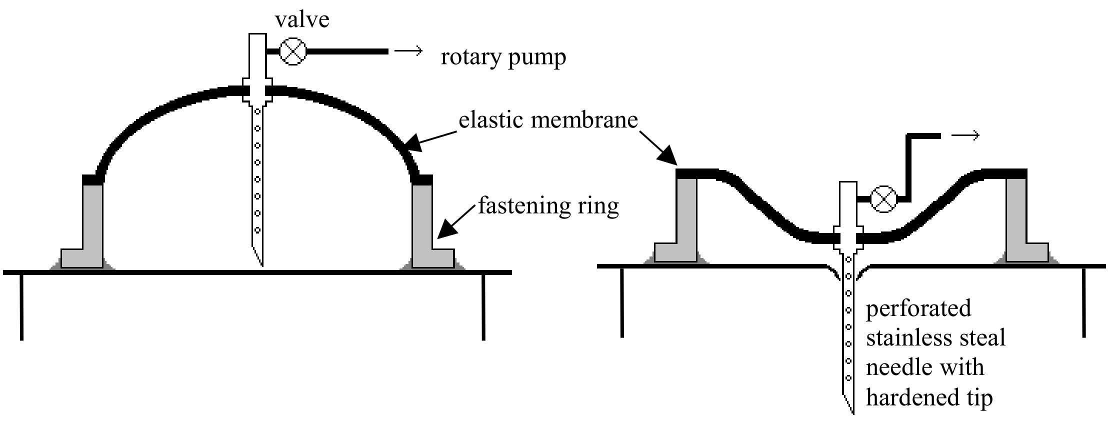
The solid (or solidified) low and intermediate level radioactive wastes temporarily stored at the site of Paks NPP are packed into 200 l stainless steal drums. Ten drums were chosen for repeated sampling: four drums contained compacted solid waste, three drums were filled with grouted sludge and three drums contained solid waste without compaction. (Formerly the L/ILW of Paks NPP was transported to a repository, so there are no conditioned wastes older then two years at the site.) The parameters of the investigated drums are given in Table. 1.

Table 1. Parameters of the investigated drums

Sample code	3.1.1 Type of waste	Time of conditioning	Max. dose rate (nGy/h)
1T	compacted	25/03/98	1200
2T	compacted	23/03/98	4200
3T	compacted	24/03/98	2800
4T	compacted	19/03/98	2500
1NT	non compacted	03/04/98	1200
2NT	non compacted	29/04/98	4500
3NT	non compacted	24/04/98	2000
1S	grouted sludge	10/05/99	2000
2S	grouted sludge	06/05/99	1800
3S	grouted sludge	08/10/99	2500

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 200 l drums are made of 1.2 mm thick stainless steal with polyethylene linen. The sampling device has to make possible the repeated sampling and prevent the escape of the gas from the drum. The sampling device can be seen in Fig. 1a. and 1b.



a) Fixing b) Sampling

Fig. 1. Sampling device

After fixing the sampling device to the top of the drum the space between the drum surface and the elastic membrane was evacuated by a rotary pump to 0.01 mbar. Piercing the lid by the needle the gas from the drum flows through the perforated tube into the sampling unit. The aerosol and dust are filtered. The sampling arrangement is shown in Fig. 2.

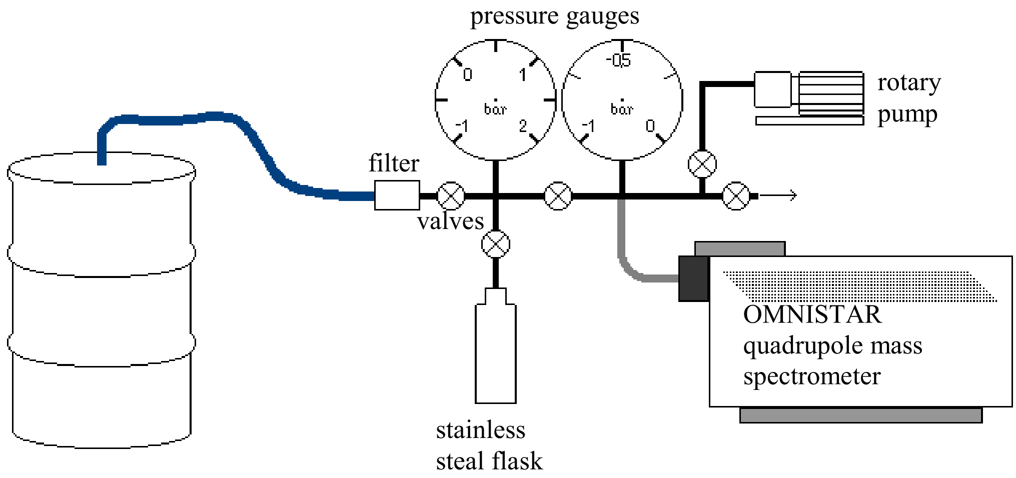


Fig. 2. Sampling and measurement of headspace gas composition

1 l gas sample was taken in stainless steal flask from each drum at each sampling time and transported to the INR/HAS for further investigations. The analysis of bulk gases was carried out in situ by quadrupole mass spectrometer.

4 RESULTS OF THE BULK GAS ANALYSIS

The drums were not evacuated after filling and closing, so at the moment of their closure they contained air above the waste. They were more or less inhermetic, the pressure inside most of them was 1 bar, except for the drum 1S in which the pressure was 1.2 bar. The composition of the headspace gases was extremely different from each other even in the case of the drums containing similar type of waste. Table 2. shows the result of the qualitative analysis of the headspace gases.

Table 2. Qualitative analysis of the headspace gases

Sample code	Composition of the headspace gases relative to the air							
	H_2	N & N_2	CO_2 & CO	H_2O	O & O_2	CH_4	NH_4	non identified
1T			+	+				
2T		+	+		--			
3T	++		+	+	X			
4T	+		?	+	--			+
1NT			+	+	-			
2NT	+		++		--			
3NT	same as the external air							
1S			+++		X	+++	+	
2S		+	+		X	++	?	
3S	same as the external air							

+ increased or present as new component;
- small decrease;
-- significant decrease
X vanished
? doubtful

No gas generation was detected in two drums (3NT and 3S), the gas composition in them was the same as of the external air.

The formation of CO_2 and the decrease of oxygen content was characteristic. The oxygen content decreased by two orders of magnitude in three drums and completely vanished from other three drums.

Hydrogen formation could be detected in three drums: 3T, 4T and 2NT. In these drums the amount of oxygen decreased at least by two orders of magnitude, in the case of 3T it completely vanished. In drums 3T and 2NT a significant CO_2 formation also could be seen. In the case of 4T the increase of CO_2 content could not been identified. In this drum a little of ammonia, a large amount of fragments of carbohydrates, all together in cc. 6% of the total gas content (Fig. 3.) were found. Each of the three drums contained excess water vapour in a small amount.

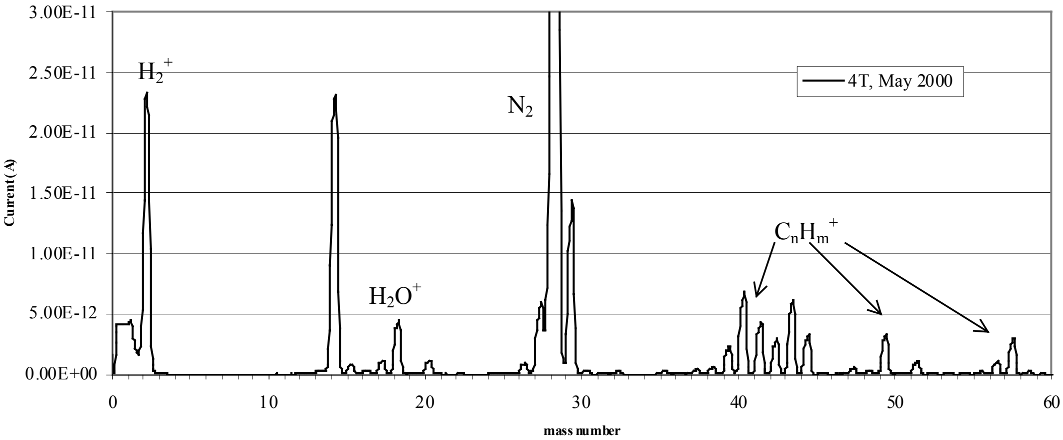


Fig. 3. Composition of the headspace gas of the drum 4T

The most dramatic changes in the gas composition were registered in drums 1S and 2S (Fig. 4. and Fig. 5.). They contain grouted sludge and they were conditioned only in May 1999. During this relatively short time a fairly high amount of methane and CO_2 was formed and the oxygen was completely depleted.

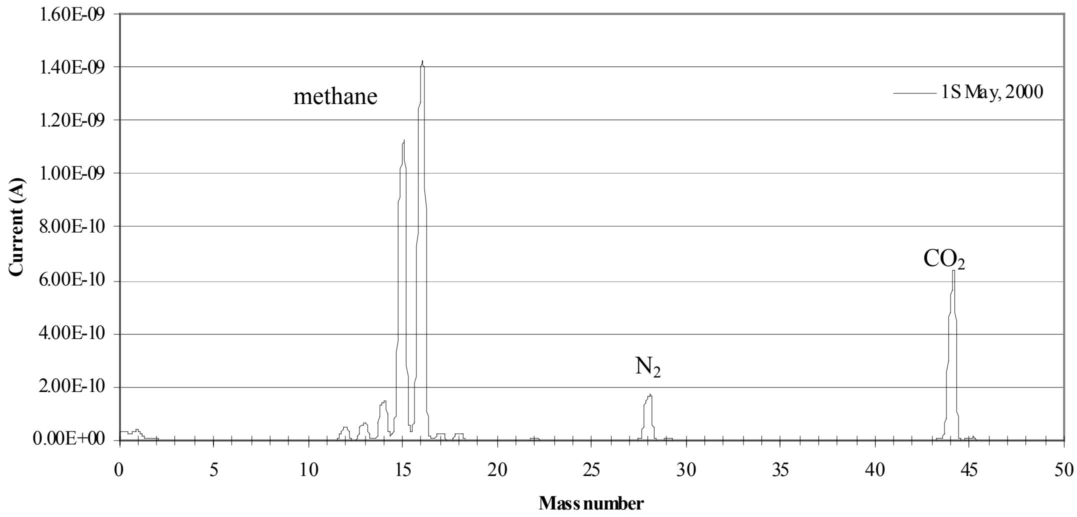


Fig. 4. Headspace gas composition in drum 1S

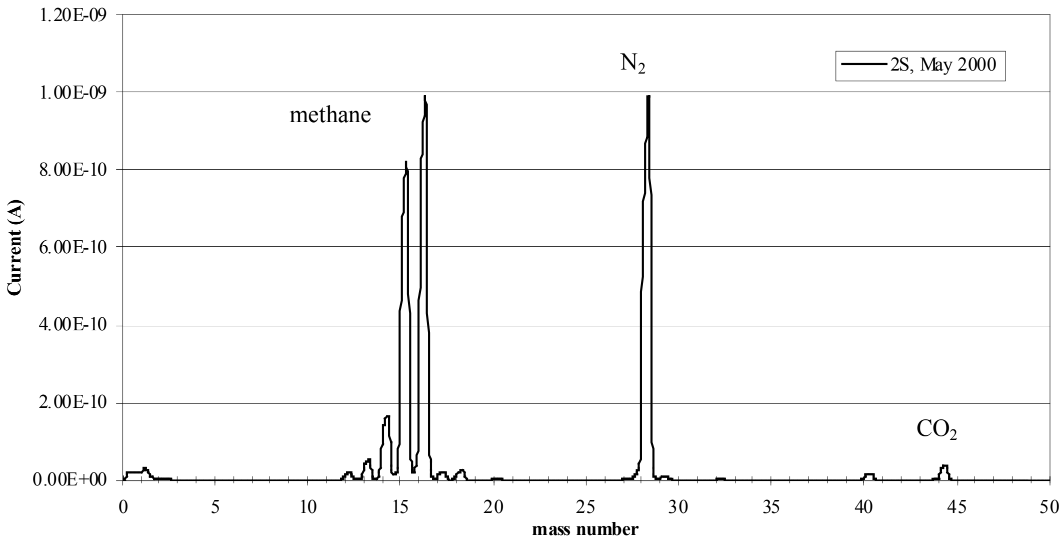


Fig. 5. Headspace gas composition in drum 2S

5 CONCLUSION

The gas compositions in the individual drums were very different. Generally the carbon dioxide was the major gas being generated and the oxygen was depleted. The formation of hydrogen could be detected in drums in which the oxygen was present in a very small amount or was completely missing. It indicates the second phase of the corrosion (anaerobic corrosion).

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. It suggests the second or third phase of the microbial decomposition.

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.

Further investigations will be needed to determine the rate and tendency of the gas generation for the individual drums and calculate the amount of the generated gases.

6 ACKNOWLEDGEMENT

This work was financed and supported by PURAM. We thank Ms. Magdolna Mogyorósi for her assistance in the sampling.

7 REFERENCES

[1] Agg, PJ, Moreton, AD, Rees, JH, Rodwell, WR and Sumner, PJ, 1993. *NSARP Reference Document, Gas generation and migration,* January 1992, Nirex Report NSS/G120.

[2] Agg, PJ, 1993. Modelling gas generation in radioactive waste repositories. *Nuclear Energy*, **32/2** (1993) 81-87.

[3] Agg, PJ, Arcus, A., Blackwood, D., Fitzgerald, P., Holtom, GJ. And Rosevear, A., 1997. Gas generation from low level radioactive waste: a comparison of model derived and experimental data. *Microbial Degradation Processes in Radioactive Waste Repository and in Nuclear Fuel Storage Areas*. (Wolfram, JH, Rogers, RD and Gazso, LG) NATO ASI Series. Kulver Academic Publishers, the Netherlands, 1997. 247-253.

[4] Agg, PJ, Nash, PJ, Rodwell, WR, Lineham, TR, 1995. Gas generation and migration from radioactive waste repositories. *Scientific Basis for Nuclear Waste Management XVII. Symposium*. (Murakami, T. and Ewing, RC) **1**. (1995) 564-574.

[5] Barlaz, MA, Milke, MW and Ham, RK, 1987. Gas production parameters in sanitary landfill simulators. *Waste Menegement and Research*, **5**, (1987) 27.

[6] Biddle, P, McGahan, D, Rees, JH and Rushbrook, PE, 1987. *Gas generation in repositories*. UKAEA Report AERE-R12291.

[7] Chan Hee Cho, Chang Lak Kim, Myung Chan Lee, Heui Joo Choi and Agg, Pj. 1996. Assessment of gas generation in underground reposirory of low-level waste. *J. Korean Nuclear Society*, **28**, (1996) 79-92.

[8] Eder, W and Lierse, Ch, 1995. Gas formation in low and medium level radioactive waste packages. *Proc. of the Fifth Int. Conf. on Radioactive Waste Management and Environmental Remediation. ICEM'95*. (Slate, S, Feizollahi, F and Creer, J). **2**, 925-927.

[9] Greenfield, BF, Rosevear, A and Williams, SJ, 1990. *Review of microbial, chemicaland radiolytic degradation of organic material likely to be present in a radioactive waste repository*. UK DoE Report No. DOE/HMIP/90/002.

[10] Halvadakis, CP, 1983. *Methanogenesis in solid-waste landfill bioreactors*. PhD Thesis, Stanford University, Department of Civil Engineering.

[11] Hoeck, J, 1983. Significance of biogas production in waste tips. *Waste Management*, **1**, (1983) 323-335.

[12] Humphreys, PN, Kelly, EJ, Binks, P and Howarth, DC, 1997. Microbial aspects of LLW disposal at the UK low level radioactive waste disposal site. *Microbial Degradation Processes in Radioactive Waste Repository and in Nuclear Fuel Storage Areas*. (Wolfram, JH, Rogers, RD and Gazso, LG) NATO ASI Series. Kulver Academic Publishers, the Netherlands, 1997. 217-232.

[13] Jefferies, NL, 1990. *The evolution of carbon-14 and tritium containing gases in a radioactive waste repository*. UK Nirex Ltd Report NSS/R198.

[14] Marsh, GP, 1988. *Progress in the assessment of the corrosion of low and intermediate level waste canisters under repository conditions*. UK Nirex Ltd Report NSS/R126.

[15] Naish, PJ, 1993. *The anaerobic corrosion of carbon steel in concrete.* UK Nirex Ltd Report NSS/R273.

[16] Rees, JH, 1989. *Gas evolution and migration in repositories: current status*. Nirex Report NSS/G112.

[17] Rees, JH and Rodwell, WR, 1988. *Gas evolution and migration in repositories: current status*. Nirex Report NSS/G104.

[18] Sharland SM and Newton CJ, 1989. *The long-term prediction of corrosion of stainless steel nuclear waste containers*. UK Nirex Ltd Report NSS/R136.

[19] Simpson JP and Weber J, 1988. Hydrogen evolution from corrosion in nuclear waste repositories. *UK Corrosion'88. Brighton UK. Proceedings*, **2**. (1988) 33-46.

[20] Sorensen, B, Jensen, PB and Maahn E, 1990. The corrosion properties of stainless steel reinforcement. *Corrosion of reinforcement in concrete*. Elsevier, 1990. 601-610.

[21] Watkiss, PR, Holtom, GJ, Rosevear, A and Holmes, R. 1993. The microbial degradation of low level waste simulant in shallow trenches and engineered concrete lined vaults. *Proc. Int. Symposium on Subsurface Microbiology*, Bath U.K. 19-24 Sept. 1993.

Yim, MS, Simonson, SA and Sullivan, TM 1996. Investigation of ^{14}C release in an