Gas Generation Rates as an Indicator for the Long Term Stability of Radioactive Waste Products

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ABSTRACT

Pursuant to the "Act on the Peaceful Utilization of Atomic Energy and the Protection against its Hazards" (Atomic Energy Act) the Federal Office for Radiation Protection (Bundesamt für Strahlenschutz, BfS) is legally responsible for the construction and operation of federal facilities for the disposal of radioactive waste.

Within the scope of this responsibility, particular due to § 74(1) Ordinance on Radiation Protection, BfS defines all safety-related requirements on waste packages envisaged for disposal, establishes guidelines for the conditioning of radioactive waste and approves the fulfillment of the waste acceptance requirements within the radioactive waste quality control system.

BfS also provides criteria to enable the assessment of methods for the treatment and packaging of radioactive waste to produce waste packages suitable for disposal according to § 74(2) Ordinance on Radiation Protection.

Due to the present non-availability of a repository in Germany, quality control measures for all types of radioactive waste products are carried out prior to interim storage with respect to the future disposal. As a result BfS approves the demonstrated properties of the radioactive waste packages and confirms the fulfillment of the respective requirements.

After several years of storage the properties of waste packages might have changed. By proving, that such changes have no significant impact on the quality of the waste product, the effort of requalification could be minimized. Therefore, data on the long-term behavior of radioactive

waste products need to be acquired and indicators to prove the long-term stability have to be quantified.

Preferably, such indicators can be determined easily with non-destructive methods, even for legacy waste packages. A promising parameter is the gas generation rate.

The relationship between gas generation rate and long term stability is presented as first result of an ongoing study on behalf of BfS. Permissible gas generation rates that ensure adequate product stability with respect to future disposal are to be identified.

INTRODUCTION

The radioactive waste disposal policy in Germany has been based on the decision that all types of radioactive waste are to be disposed of in deep geological formations. Near-surface disposal or shallow land burial is not practiced in Germany because of the high population density and climatic conditions; furthermore appropriate deep geological formations exist.

In the former GDR, the Morsleben repository was available for the disposal of low- and medium-level radioactive waste since 1971. Subsequent to German reunification, this repository was used for the emplacement of low- and medium-level radioactive waste (37,000 m^3 in total) from all over Germany up until September 1998. The licensing process for the closure of the Morsleben repository started in the nineties. The main licensing document, the so-called Plan, has been provided – together with the Environmental Impact Assessment and further important documents – to the competent regulatory body (licensing authority) on 13 September 2005. The licensing procedure is in progress and present activities are particularly focused on the final preparation of further documents for the licensing authority.

In 1982, an application was submitted to dispose of non-heat generating waste at the Konrad mine, i.e., a former iron ore mine. The license was issued on 22 May 2002 for 303,000 m^3 low- and medium-level radioactive waste. However, the decision is not legally valid since objections have been filed. After final court decision confirming the license and the decision of the Federal Government it will take several years until the emplacement of radioactive waste in the Konrad repository can start. In parallel to the licensing procedure, since many years, the Konrad waste acceptance requirements /1/ and, pertinent to these requirements, the Konrad radioactive waste quality control measures /2/ are successfully applied. Nevertheless, final approvements on the waste package disposability are still to be made.

Due to the non-availability of a repository in Germany, radioactive waste products and packages have to be stored for a period of one or two decades until they can be disposed of. Some of the waste packages in the German interim storage facilities were treated ten to twenty years ago. The properties of the waste packages may change during the period of interim storage. Degradation mechanisms may include corrosion of the container, deterioration of the waste form, general loss of waste package integrity, etc. and particularly affect the physical or chemical properties of the waste form. These mechanisms are principally influenced by the chemical characteristics of the waste form. A stable waste form is very important if long-term storage is required. In this case, slow degradation over extended periods of time may result in a waste form that no longer meets disposal acceptance criteria. In this case, future reconditioning may be required to ensure that the waste form meets the waste acceptance requirements at the time of disposal. In any event, the package or waste form must be in a suitable state for safe retrieval at the end of the storage period (e.g., physically intact and safe to handle) and it must meet the requirements for transport as well as for subsequent phases of waste management /3/.

Therefore, BfS started an investigation of possible changes of the relevant waste package properties due to storage time and started to look after indicators for those deteriorations. The key degradation products include gases and liquids. Because of the good accessibility the first parameter to be examined is the gas generation as a possible indicator for chemical and biological processes inside the waste packages.

QUALITY CONTROL OF WASTE PACKAGES IN GERMANY

In performing its federal supervision, the Federal Ministry for Environment, Nature Conservation and Nuclear Safety (Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit – BMU) is supported by the Federal Office for Radiation Protection (Bundesamt für Strahlenschutz - BfS) in all matters concerning nuclear safety and radiation protection. The responsibility for the disposal of radioactive waste lies with the Federal Government, BfS being the legally responsible authority. Therefore, all methods for the treatment of radioactive waste and for the conditioning of waste packages for disposal have to be approved by BfS. Complementary the waste treatment has to be qualified for disposal due to the German Radiation Protection Ordinance by BfS. The evaluation of reports for the qualification of waste treatment processes for storage and disposal is done by experts of TÜV EnSys Hannover on behalf of BfS.

The waste generators and service companies demonstrate the characterization and treatment of the radioactive waste in a process sequence plan. This qualification plan describes each planned waste treatment step and defines the tasks and the responsibilities of the different parties involved. It is submitted to the federal authority, the Federal Office for Radiation Protection (BfS) and to Federal State authorities responsible for the interim storage. Additionally the TÜV EnSys Hannover experts perform an assessment on behalf of BfS to verify the suitability of the waste products and waste packages for disposal in general on the basis of the Konrad waste acceptance requirements /1/.

The properties of the treated waste are documented. These documentations of the waste packages will be checked by the TÜV EnSys Hannover experts. After verifying the compliance of the waste properties with the Konrad waste acceptance requirements approval is given by BfS.

GAS GENERATION IN RADIOACTIVE WASTE PACKAGES IN GERMANY

In the course of inspections of German interim storage facilities in 1987 and in the following years waste packages with a build up of pressure due to the development of gases were detected. Nearly all these packages contained radioactive waste with low contamination of beta and gamma emitters. A gas production due to radiolysis or due to production of helium could be excluded. Investigations in different laboratories showed the following main reasons for gas production:

- Biological degradation of organic compounds in low-active waste with the production of carbon dioxide and methane,
- Corrosion of metals due to chemical reactions with humidity and the production of hydrogen,
- Reaction of ashes from the combustion of low-level combustible waste with humidity resulting in the generation of hydrogen and methane from residues of metals and aluminum carbide,
- Reaction of amphoteric metals like aluminum or zinc with concrete, producing hydrogen.

With the exception of the last example all these reactions start with the consumption of oxygen, resulting in generation of non-burnable mixtures of hydrogen and oxygen inside the package. Most of the interim storage facilities in Germany are sufficient aerated, i.e. explosive gas mixtures can be excluded. However, the generation rate of burnable gases was limited for the

disposal at the Morsleben site to 5 ml / m^3 h. Additionally, the generation of all gases is an indicator of reactions within the waste product and has to be avoided. Since 1988 the treatment of low-active waste was modified in order to prevent the gas generation. An increasing amount of the waste was sorted, metallic waste was melted, residues from the combustion were no longer cemented, low-active waste was dried and compacted waste was inspected for liquids. These changes in the treatment are documented in the process sequence plans. To certificate the success of these activities to avoid gas generation, gas samples were taken from the packages and analyzed.

EVALUATION OF GAS ANALYSES

Radioactive low-level waste in Germany usually is packed in 200-l-drums or in box-shaped sheet steel containers. The 200-l-drum can easily be closed tightly; the containers have in most cases an unknown leakage. To obtain reliable estimates of the quantities and rates of the gas production in low-level waste most of the measurements were carried out using 200-l-drums. Quantitative gas component analyses of headspace gases of drums were executed by gas chromatographs. Through the gasket of the drums a sample is taken with an injection needle and this sample is transferred to the gas chromatograph. The analyzed gas components are oxygen, nitrogen, hydrogen, carbon monoxide, carbon dioxide and methane. The time span between closure of the containers and collecting the samples has to be longer than ten days. The detection limits are in a range of approximately 0.1 vol.-%. The gas generation rate in the stored low-level waste was calculated using the data on composition of the gas, the time span between closure of the drum and the sampling as well as an estimated volume of the headspace in the drum.

As TÜV EnSys Hannover is involved in the quality control of radioactive waste packages by performing the assessments of waste packages for storage and disposal; the documentations of waste packages with the results of gas analyses are available to the TÜV EnSys experts. In total, over 4,500 results were collected and sorted in different categories in relation to the origin of the waste, to the kind of waste container, to the waste composition and to the treatment of waste. The following table demonstrates some of the different compositions, treatments and origins of the waste.

Table I: Samples of Low-level Waste and Gas Generation Rates

Origin	Waste type	Nr. of samples	H_2 ml/m^3 h		CH_4 ml/m^3 h		CO_2 ml/m^3 h	
			Maximum	Median	Maximum	Median	Maximum	Median
NPP	Organic	280	130	0.03	16	0.00	63	0.05
NPP	Combustion residues	94	77	0.08	10	0.00	0.6	0.00
NPP	Melting residues (slag)	44	41	0.54	15	0.00	2.2	0.08
NPP	Inorganic	175	285	0.11	10	0.00	28	0.03
NPP	Dry waste	2,078	1,080	0.61	240	0.00	165	0.00
NPP	Metals	600	285	0.00	24	0.00	63	0.00

More than 3,000 findings of gas analyses result from wastes from nuclear power plants (NPP). Other waste producers like fuel element producers and research institutes generated less waste and, therefore, less information concerning gas generation are available. More than 2,000 collected values of gas composition were generated by analyses from dry solid waste from operating nuclear power plants. Other important waste products are compacted organic wastes, compacted metals, residues from the melting of contaminated iron and steel, compacted residues from the incineration of low-level waste and compacted inorganic waste. Table I shows the median and the maximum values of the generation rates of carbon dioxide, hydrogen and methane for these types of wastes.

Regarding the median values of gas generation most of the German low-level waste is stable with low chemical and biological activities in the waste product. Therefore, for the most part of radioactive waste to be disposed of, degradation is not a problem. However, the maximum values of gas generation expose the existence of a small number of waste packages with insufficient properties. Figure 1 demonstrates the distribution of waste packages with different gas generation rates.

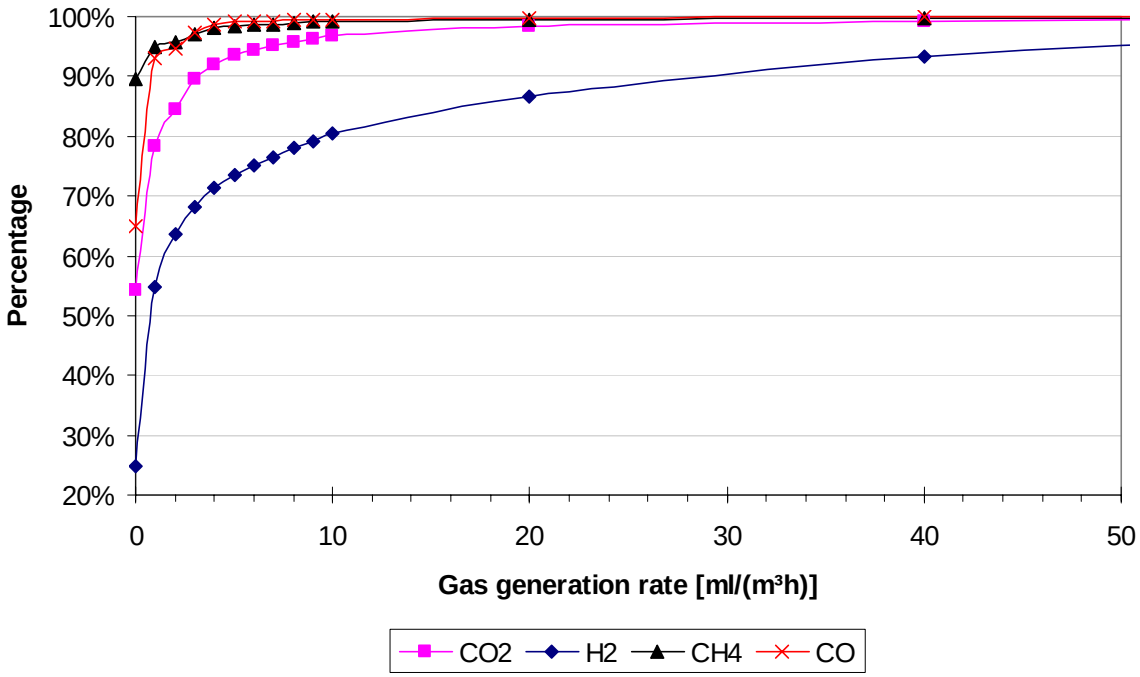

Fig. 1: Distribution of gas generation rates of compacted dry waste

More than 80 % of all sampled waste packages with compacted dry waste (unsorted organic and inorganic operational waste from NPPs) generate less than 10 ml hydrogen per hour and cubic meter of waste. The hydrogen generation is caused by corrosion processes in the waste between metals and small amounts of humidity. The hydrogen generation starts after consumption of oxygen and decreases usually after several weeks. Waste packages with high hydrogen generation rates (e. g., > 20 ml/ (m^3 h)) are dried. According to this rather simple measure lower hydrogen generation rates are obtained. The distribution of the generation rates for carbon dioxide and methane - more than 80 % of all waste packages generate less than 1 ml/ (m^3 h) of CO_2 and CH_4 - demonstrates that in most cases microbiological processes can be neglected.

CONCLUSION

Approximately 4,500 results of gas analyses from the headspaces of waste packages with German low-level waste are examined and evaluated. The results showed differences due to the composition of the waste. Independent of the waste composition the results confirmed a sufficient stability of a great number of the investigated waste products concerning the suitability for disposal. A small percentage of the waste packages give evidence for an inadequate stability.

These packages have to be treated,, e. g. by drying. Subsequent to this step the properties of the waste are to be assessed again.

The gas generation rate is used as an indicator for the long-term stability of waste products in the process of quality control of waste packages in Germany. An evaluation of more than 4,500 gas analyses demonstrated the efficacy of this procedure.

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