# GAS GENERATION AND RELEASE IN DEEP GEOLOGICAL RADIOACTIVE WASTE REPOSITORIES

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## ABSTRACT

Whereas the subject of gas generation and possible gas release from radioactive waste repositories has gained in interest on the international scene, the Commission of the European Communities has increased its research efforts on this issue. In particular in the 4th five year R&D program on Management and Storage of Radioactive Waste (1990-1994), a framework has been set up in which research efforts on the subject of gas generation and migration, supported by the CEC, are brought together and coordinated. In this project, called PEGASUS, Project on the Effects of GAS in Underground Storage facilities for radioactive waste, about 20 organizations and research institutes from 7 European countries are involved.

The project covers both experimental and theoretical studies of the processes of gas formation and possible gas release from the different waste types, LLW, ILW and HLW, under typical repository conditions in suitable geological formations as clay, salt and granite.

In this paper an overview is given of the various studies undertaken in the project as well as some first results presented.

## INTRODUCTION

The Commission of the European Communities has in its 4th five year R&D program on Management and Storage of Radioactive Waste, 1990-1994 (1) launched an international Project on studies of the Effects of GAS in Underground Storage facilities for radioactive waste, known as the PEGASUS project, in which the Commission is co-funding research carried out in approximately 20 laboratories in Belgium, France, Germany, Italy, The Netherlands, Spain and the United Kingdom. The project covers both experimental and theoretical studies on the processes of gas formation and possible gas release from the different waste types (LLW, ILW and HLW) under typical repository conditions in potential host rocks such as clay, salt and crystalline rock. Moreover, the Commission has created a forum in which specialists involved in the various research activities meet regularly to discuss the topics and the progress made (2).

The proceedings of annual progress meetings are being published in the EUR series (3). The following is an overview of the various studies undertaken, while more details and results can be found in Ref. 3.

## GAS GENERATION MECHANISMS

Gas generation may occur in a deep geological radioactive waste repository due to several phenomena depending on a number of factors such as the nature of the waste, the waste package, buffer and backfill material and the host rock.

Corrosion of the waste package has been recognized as one of the most important phenomena. Corrosion which can occur either as a generalized or as a localized process, depends on the nature of the container, the chemical properties of the environmental water and the physical conditions. Another phenomena is the effect of radiation which may effect the waste matrix (internal radiolysis) and/or the near field (external radiolysis). Internal radiolysis is mainly due to alpha and (partly) beta radiation, whereas for external radiolysis only gamma radiation has to be considered.

Gas production can also come from microbial degradation of organic matter existing in the waste form, near field and groundwater. Finally, temperature increases, in particular for disposal of heat generating waste, will lead to consequences on gas production and especially on the transformation of water into vapor. Moreover, generation of natural gases may be enhanced by increased temperatures within the repository.

## GAS GENERATION STUDIES

In a three year (1992-1994) joint study undertaken by ANDRA (F), ENRESA (E) and GRS (D), a description of the gas formation mechanisms which are relevant in different waste repositories will be performed. The waste forms considered are medium level waste, vitrified high level waste and spent fuel from light water reactors. Two types of geological formations are covered : granite and salt. Calculations will be performed for the repository conditions defined concerning gas production rates, gas transport and gas release.

In parallel, a joint experimental research program is being performed by CEA-Cadarache (F) and AEA-Harwell (UK). Waste packages studied are resp. cemented alpha waste, bitumized waste (type STE 3) and inactive samples of cements CPA 55, CLC 45 and concrete structural materials. Gas release ($H_2$, $O_2$, $N_2$, Tritium) due to internal radiation in active cemented alpha waste packages and due to external radiation (Co-60 source) of samples of inactive cements and bitumen containing organic components (EDTA and TBP) are investigated. Gas production due to anaerobic microbiological degradation is studied on bitumized waste of the type STE 3. Finally, biocorrosion of cements (CPA 55 and CLC 45) by autotrophic and heterotrophic microorganisms will be studied as well as behavior of concrete structural materials with respect to biodegradation.

In the Asse salt mine in Germany two major waste emplacement demonstration tests are planned to be implemented. They concern retrievable emplacement of intermediate level waste and spent fuel of the High Temperature Reactor (MAW/REV project) and a test disposal of high radioactive sources, simulating vitrified high level waste (HAW project) (4).

In the MAW/REV project, six ILW packages comprising 200 l drums containing hulls, spent fuel hardware and dissolver sludges from the reprocessing plant WAK at Karlsruhe, grouted in cement, and four 220 l stainless steel canisters each containing 950 spent pebble bed fuel elements from the AVR high temperature reactor at Jülich, are to be emplaced in the Asse salt mine. The waste packages (see Table I) have been investigated for the release of radioactive gaseous (Kr-85, HTO, HT and C-14) and in the case of the intermediate level waste for the formation of hydrogen due to radiolytic disintegration of the water content of the hardened cement paste. The release rates of the ILW steel drums are averaged values from several years of a measuring program. For the monitoring of the gas release during the emplacement, a gas control and analysis station has been installed in the Asse mine. The test emplacement is suffering delays due to licensing aspects.

In the framework of the HAW project, laboratory investigations have been undertaken on the gas generation from salt due to temperature and radiation effects. At GSF-Braunschweig (D) salt samples from the Asse mine with a mass of 1 to 5 kg were introduced into gastight sealed glass containers with a volume of about 5 liters. The containers were then purged with pure nitrogen via two septa following which they are stored either at room or at elevated temperatures of up to 300°C. Gas samples are taken via the septa using a syringe and are analyzed by gas chromatography or mass spectrometry. The maximum values of the gases released from 100 Stassfurt-and Leine-halite samples at a temperature of 300°C are shown in Table II. The components $CO_2$, $H_2S$ and the gaseous hydrocarbons are initially present, whereas the quantity of HCl is generated by thermal decomposition of some trace minerals such as bishofite or carnallite.

A more intensive experimental program on radiolytic gas production has been conducted by ANDRA (F) (5). A large number of salt samples from the Asse mine has been irradiated in the OSIRIS reactor facility at Saclay. Various parameters significant for gas production were investigated such as the mineralogical composition of the samples and the gases initially present before irradiation, gamma dose rate and gamma spectrum and integrated dose (see Table III). About 200g of the salt samples to be investigated were put in pyrex glass ampoules; the free volume to salt volume ratio was 3. The results obtained showed that the main compounds produced in the presence of oxygen are $CO_2$, $N_2O$, $H_2$ and $CH_4$. Knowledge of the mineralogical and chemical composition of the salt is of prime importance in determining the origin of the gaseous compounds formed. An impure salt containing more organic matter and fluid inclusions will cause higher production of gas. From the tested parameters it appeared that the integrated dose has a great influence on the quantity of formed gas. For high doses ($>10^7$Gy) the generation of active compounds was noticed (HCl, $Cl_2$, $SO_2$, $H_2S$ etc.). However, varying the dose rate $10^2$ to $10^5$ Gy/h had no significant effect on produced gas quantities. Variation of the temperature, 50-250°C, had only a slight effect on all compounds.

## SEALING SYSTEMS

According to numerous repository design concepts the heat generating waste canisters will be disposed of in deep disposal boreholes. The waste canisters will be stacked vertically in the boreholes on top of each other and the borehole sealed. For reasons of safety the borehole seal is to be designed in such a manner that an unacceptable increase of borehole gas pressure and an uncontrolled release of gases and radionuclides into the repository are avoided. These requirements are contradictory in principle, but have to be considered during the development of borehole seals. In a joint study between GSF-Institut für Tieflagerung (Germany) and The Netherlands Energy Research Foundation (ECN-NL) appropriate borehole seals for repositories in salt are being developed and will be tested in a second phase. The materials considered suitable are to be resistant against temperature, rock mass pressure and deformation. Also the

**TABLE I**

Specification Data of the Waste Packages to be Used for the MAW Retrievable Emplacement Test (MAW Project) and Data on Radiolytically Produced Hydrogen

| | Dissolver Sludges | Cladding Hulls | Fuel Hardware | HTR-Fuel Elements |
|---|---|---|---|---|
| Number of Packages | 3 | 2 | 1 | 4 |
| Type of Package | 200-l steel drum | 200-l steel drum | 200-l steel drum | 220-l stainless steel canister |
| Designation of the Waste Packages | FKS-1<br>FKS-2<br>FKS-3 | H-187<br>H-190 | S-190 | AVR-TL-K 1<br>AVR-TL-K-2<br>AVR-TL-K-3<br>AVR-TL-K-4 |
| Overall Mass of the Packages in kg | ≤300 | ≤340 | ≈320 | ≈350 |
| Overall Mass of the Waste in kg | ≤0.14 | ≤74 | ≈49 | ≤180 |
| Overall Uranium Content in g | <13 | <320 | - | <403 |
| U235-/U233- content in g | $<63*10^{-3}$/- | <2/- | - | <124/89 |
| Overall Plutonium Content in g | <0.54 | <3 | - | <8.5 |
| Pu239-/Pu241- Content in g | ≈0.30/<0.06 | <2/<0.3 | - | <1.7/0.4 |
| Radiolytically Generated Hydrogen ml/d | 28<br>77<br>65 | 6.4<br>2.2 | 85 | - |

**TABLE II**
Gas Release at a Temperature of 300°C. Maximum Values Observed with 100 Salt Samples from the Asse Mine

| | |
|---|---|
| $CO_2$ | up to 400 ppm = 45 Nl/m$^3$ salt |
| $H_2S$ | up to 5 ppm = 6 Nl/m$^3$ salt |
| HCl | up to 150 ppm = 195 Nl/m$^3$ salt |
| gaseous hydrocarbons especially $CH_4$ | up to 60 ppm = 156 Nl/m$^3$ salt |

**TABLE III**
Radiolytic Gas Generation in Salt; Test Parameters

| Parameter | Values or nature |
|---|---|
| Dose rate | $10^2$ to $10^5$ Gy/h |
| Integrated dose | $10^2$ to $10^7$ Gy |
| Grain size | 0.125 mm to 50 mm |
| Temperature | Ambient to 250°C |
| Filling gas | Vacuum, He, Ar, and different ratio of $N_2/O_2$ |
| Mineralogy | Asse salt, pure minerals |
| Container material | Various steel alloys |

chemical stability of the sealing materials is of significance. A radiation influence on the borehole seal does not have to be taken into account as a radiation shielding effect is exerted by the covering layer above the waste packages as well as by the lower part of the plug. This aspect is therefore considered negligible. From a literature survey it has been concluded that salt grit, salt bricks, salt cement and bentonites seem to be most suitable. The properties of these materials and the behavior of seals and seal components under the special HLW borehole disposal conditions in rock salt will be further investigated. Moreover, emplacement techniques and quality assurance topics will be analyzed.

Multicomponent constructions for sealing of boreholes and galleries are considered as well. In the Asse salt mine, the construction of a multicomponent dam consisting of a hydraulic sealing system, a long-term seal and a static abutment is underway. Due to the short test period on the entire test dam of some years only proven experimental evidence of functioning can be provided for the hydraulic sealing system of the dam construction. In order to obtain also reliable information on the development of porosity and permeability of the long-term seal a separate test is scheduled.

The long-term seal component will consist of salt bricks made of compressed salt grit and bond together with a special mortar consisting of salt powder, salt clay and brine. It has to meet the following requirements:

- contribution towards the mechanical integrity of the entire construction
- mechanical behavior similar to the surrounding rocksalt
- long-term corrosion resistance against brines and gases
- low permeability at the outset of functioning, corresponding to the surrounding rock salt
- mechanical stability and decreasing permeability up to a time period of 500 years.

The permeability of the long-term seal component, along the interface with the rocksalt and of the disturbed rock zone has to be investigated. The changes to be investigated in particular are the development of permeability as dependence upon mechanical load and the physico-chemical processes under the influence of brines and/or gases versus time.

## MIGRATION OF GASES THROUGH HOST ROCKS

Within the project PEGASUS, migration of generated gases through geological barriers will be studied on the three host rocks considered: salt, clay and crystalline rock. We have already mentioned above some investigations being carried out in the Asse salt mine in Germany. In-situ experimental work on gas permeability of salt will also be performed in France in a bedded salt layer in a potash mine. Two successive experiments will be carried out: a first one will use brine which will be injected under increasing pressure up to hydraulic fracturing of the salt massive, followed by a second one using firstly brine and then gas. The objective of this second test is to measure the gas permeability of bedded rock salt previously submitted to a brine percolation.

Gas flow experiments on clay are being performed by SCK/CEN at Mol, Belgium. To determine the gas permeability as function of the degree of saturation, first a series of gas flow experiments was carried out on artificial clay plugs with different degrees of saturation but with a dry density of 1.7 g/cm$^3$, which is the same as the Boom clay, considered as potential host rock for a geological repository in Belgium. The gas used was Argon. The relative gas permeability of about 40 clay plugs has been measured with a saturation range between 0% and 90%. The permeability decreases strongly at saturation rates above 50% and seems to become 0 at a saturation of about 90%. At this saturation no continuous gas channels remain available and the gas breakthrough pressure becomes $>0$. Breakthrough experiments were performed on clay plugs prepared from natural Boom clay. First the hydraulic conductivity of the clay plug was measured and then gas was injected at the top of the clay plug at a pressure difference below 1 MPa. The pressure difference is gradually increased until breakthrough occurs. Results have shown that there is a relationship between hydraulic conductivity and breakthrough pressure (Table IV). Furthermore, it has been found that there is a certain anisotropy of the Boom clay which means that at pressures of about 1 to 1.5 MPa gas will flow rather in the horizontal direction and not in the vertical direction. These laboratory experiments will be followed by in-situ gas injection experiments in the underground research facility HADES in the Boom clay at Mol (B). The experiments will be used to validate computer codes on the dynamics of bubble flow in saturated porous media and two phase flow codes. Modelling efforts are also undertaken to assess hydraulic and mechanical effects such as possible fracture initiation due to gas pressure build up.

## SIGNIFICANCE OF GAS GENERATION FOR REPOSITORY SAFETY

When assessing the significance of gas generation for the safety of a geological radioactive waste repository, one should first distinguish between safety during the operational phase and the post operational phase. During the operational phase,

**TABLE IV**
Results of the Breakthrough Experiments in Boom Clay

| Plug Height cm | Density $kN/m^3$ | Orientation | Hydralic Conductivity $m/s.\ 10^{-12}$ | Break-through Pressure MPa | Maximum Pore Radius $m.10^{-9}$ | Flow $10^{-4}$Nml/min |
|---|---|---|---|---|---|---|
| 4.25 | 20.29 | vertical | 2.3 | 2 | 49 | NA* |
| 4.435 | 20.60 | vertical | 1.7 | 2.45 | 41 | 170 |
| 5.255 | 20.17 | horizontal | 3.6 | 1.2 | 82 | 35 |
| 5.00 | 20.40 | vertical | 1.8 | 1.5 | 66 | 3400 |
| 4.71 | 20.24 | NA* | 2.1 | 0.9 | 110 | 460 |
| 2.765 | 20.38 | vertical | 3.4 | 2.2 | 45 | 7.1 |
| 5.00 | NA | 45° | 7.4 | 1.4 | 71 | 28 |
| 3.575 | NA | horizontal | 7.5 | <1.5 | >66 | NA |
| 3.20 | NA | NA* | 3.3 | 2.4 | 41 | 2.2 |
| 3.995 | 20.82 | artificial plug | 1.5 | 2.9 | 34 | 1.1 |

NA* : not available

gas production may lead to the formation of explosive or toxic gas mixtures. During this phase, which usually will not exceed a period of 50 years, the total volume of gas generation will however be limited. Moreover, it can rather easily be monitored and remedial actions undertaken if necessary.

During the post-operational phase various scenarios depending on the host rock and the repository design should be considered. If the near field is highly impermeable then any gas production would lead to a gas pressure build-up and potential destruction of barriers. However, in that situation there would be almost no water inflow, thus reduced corrosion phenomena and reduced gas production. The formation of a gas bubble around the waste form would prevent further fluids contacting the waste.

If the near field is permeable then a possible scenario could be that the formed gas dissolves first in the groundwater supposed to saturate the buffer and backfill materials, then moves by molecular diffusion and advection. If the gas flow rate is great enough the solubility limit will be reached and free gas will begin to migrate if the gas pressure is sufficient to overcome the capillary forces. The gas velocity will then be controlled by the absolute permeability, relative permeability, effective porosity and capillary pressure distribution of the host rock. Therefore gas formation could increase fluid transport and radionuclide migration. In the PEGASUS project some of these scenarios for generic repository designs will be assessed.

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