

GAMMA-RADIOLYTIC GAS PRODUCTION IN GROUND ROCK SALT OF HOMOGENEOUS COMPOSITION

N. Jockwer, H. Sprenger, K.-H. Feddersen, J. Mönig

ABSTRACT

Natural rock salt samples, that are representative for a repository in the salt diapirs in northern Germany, have been γ -irradiated at the High Flux Reactor (HFR) at Petten, The Netherlands, using spent fuel elements. The γ -radiolytic formation and release of gases was studied by gas chromatography. Radiation doses varied between 10^6 and 10^8 Gy, while the effect of temperature was investigated between 100 and 250 °C. The gas atmosphere in which the rock salt is irradiated has a significant influence on the product composition. When the irradiations were carried out in synthetic air, N_2O , CO, CO_2 , as well as some H_2 were detected. Under a helium atmosphere H_2 , CH_4 , and CO_2 were observed as gaseous products, while no CO or N_2O was detected. From our data, it is concluded that the contribution of the γ -radiation-induced gas formation to the total source term of gas production in an emplacement borehole for vitrified high level radioactive waste should be negligible. Other processes such as the formation of hydrogen via corrosion and the pressure increase due the creeping of the salt are much more important for the safety considerations.

1. INTRODUCTION

The emplacement of canisters containing vitrified reprocessed high level radioactive waste in boreholes in rock salt will result in an exposure of the host rock to temperatures up to 200 °C and gamma dose rates of 1000 Gy. The total dose in a repository is estimated to be in the order of 10^9 Gy. Apart from the development of radiation damage in rock salt, γ -radiation leads to the formation and release of gases from the rock salt. The processes of gas formation are of interest as they may lead to a pressure build-up, and to the formation of explosive and/or corrosive gas mixtures in sealed repository areas [Brewitz and Mönig, 1992]. Gases may also provide a means of transportation for radioactive nuclides.

In order to be able to design repositories and to assess their long-term safety, it is necessary that all sources contributing to the generation and release of gases are known qualitatively and quantitatively. Several different processes account for the gas generation and contribute to the total source term for gas production in the emplacement of high level radioactive waste. These include the gas release from the rock salt at ambient and elevated temperatures, the gas generation from the emplaced waste, e.g. via corrosion of the waste canisters, and the radiation-induced gas generation. The extent to which each of these processes contributes to the total gas generation rate depends on various factors, i.e. the waste type, the host rock and the specific disposal conditions.

The question of γ -radiation-induced gas formation and release from rock salt was addressed in some detail in previous studies [Jockwer, 1983, Jockwer and Gross, 1985, Jockwer and Mönig, 1989]. It was also the subject of another irradiation program, that was carried out in collaboration with ANDRA and CEA-SACLAY [see articles 5 and 14, this volume]. The present irradiations were meant to determine the radiation damage in natural rock salt samples from the Asse salt mine (Remlingen, Germany) [Mönig et al., 1995 (article 16, this volume)]. However, since these irradiations were carried out in sealed glass ampoules, it seemed worthwhile also to measure the radiation-induced gas formation and release in these samples for comparison with previous data. Here we report on these results. The experimental methodologies are described in detail elsewhere [Mönig et al., 1995 (article nr. 8, this volume)].

2. RESULTS

The gas atmosphere in which the rock salt is irradiated has a significant influence on the product distribution. When the irradiations are carried out in synthetic air, N_2O , CO , CO_2 , as well as some H_2 were detected. Under a helium atmosphere H_2 , CH_4 , and CO_2 were observed as gaseous products, while no CO or N_2O was detected. Other aliphatic hydrocarbons than CH_4 (e.g. C_2H_6) were also found but only in very small quantities (< 0.01 ppm), so that the individual results are not given here. H_2S was not detected in any sample.

The obtained product quantities depend on the absorbed dose and on the temperature. The dose dependence of the various gases at $100^\circ C$, $150^\circ C$, $200^\circ C$, and $250^\circ C$ are shown in Figs. 1 - 3 for irradiations in helium and in Figs. 4 - 7 for irradiations in synthetic air, respectively. The gas yields are expressed in ppm, i.e. as mg gas per kg rock salt. They were calculated from the measured gas phase concentrations using the ideal gas law as follows:

$$y = \frac{GPV_{total} \cdot GPC \cdot MW}{MV \cdot m_s} \quad (1)$$

where:

- y = yield [$\mu l/g$]
- GPC = measured gas phase concentration [$\mu l/l$]
- GPV_{total} = volume of gas phase in total system [l]
- MW = molar weight of gas component [g/mol]
- MV = molar volume of ideal gas at $25^\circ C$ (24.465 l/mol)
- m_s = mass of rock salt in the ampoule (300 g)

The data for N_2O are only given in relative units, as no test gas mixture was available for calibration during the experiment. However, the absolute yields can roughly be estimated using the response factors for hydrogen and oxygen, which are also detected on this chromatographic channel, and taking the differences in the heat conductivity of the various gases into account. On this basis a N_2O -yield of 1000 (rel. units) corresponds to a gas phase concentration of about 6 Vol-% N_2O in the glass bulb that was used for the gas measurements.

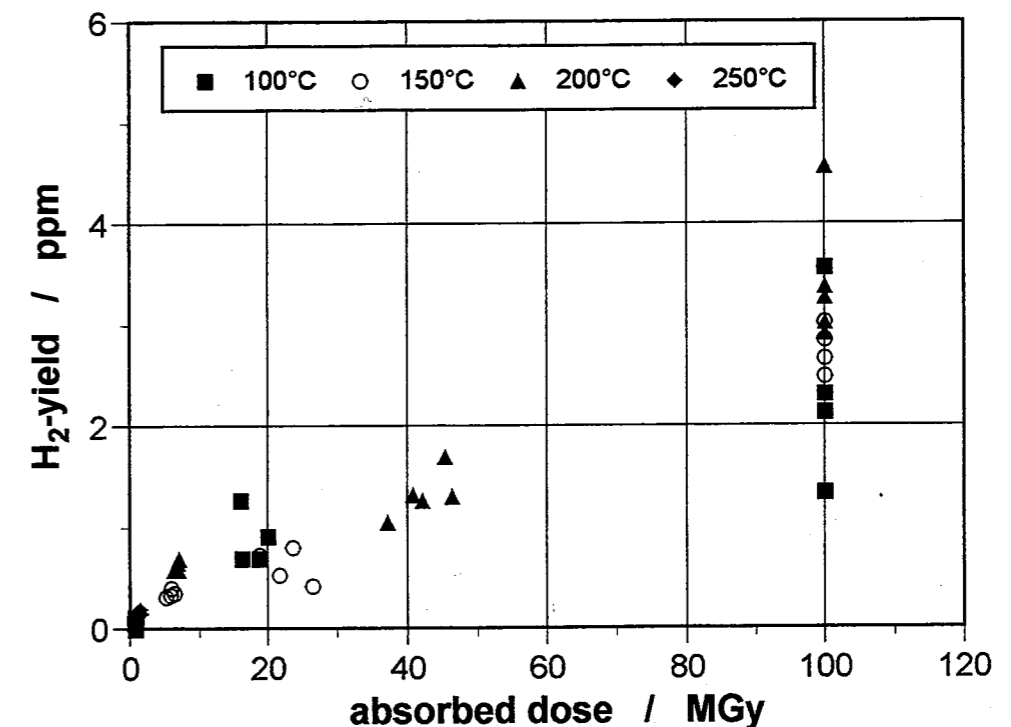


Figure 1: Yield of hydrogen vs. absorbed dose at various temperatures for γ -irradiated rock salt in a helium atmosphere.

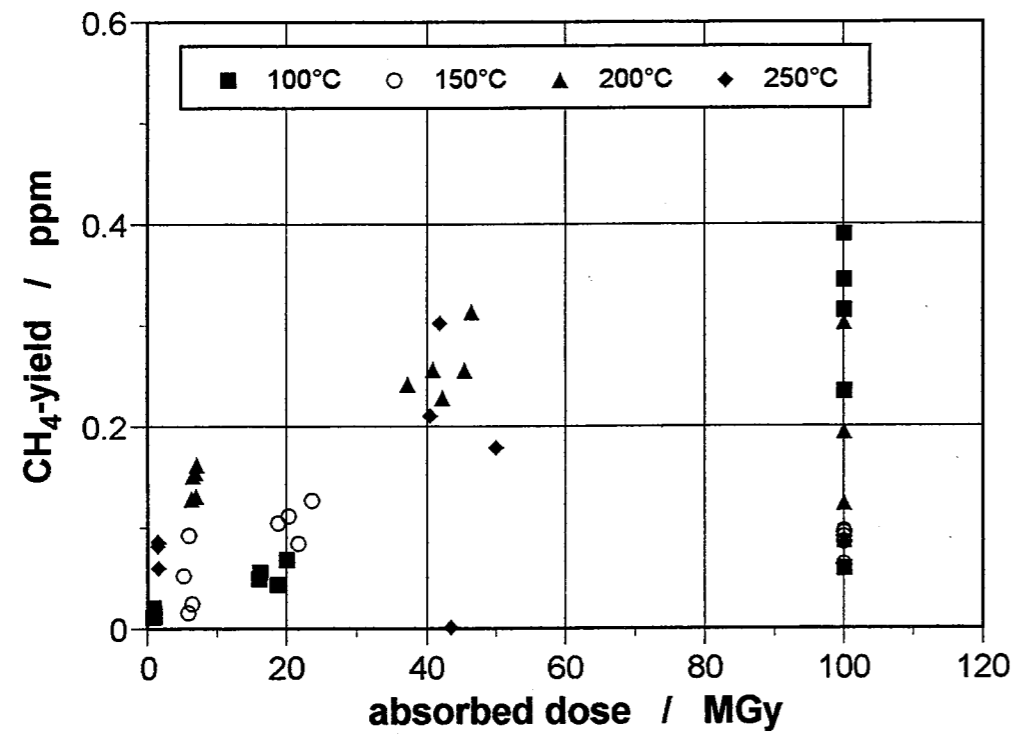


Figure 2: Yield of methane vs. absorbed dose at various temperatures for γ -irradiated rock salt in a helium atmosphere.

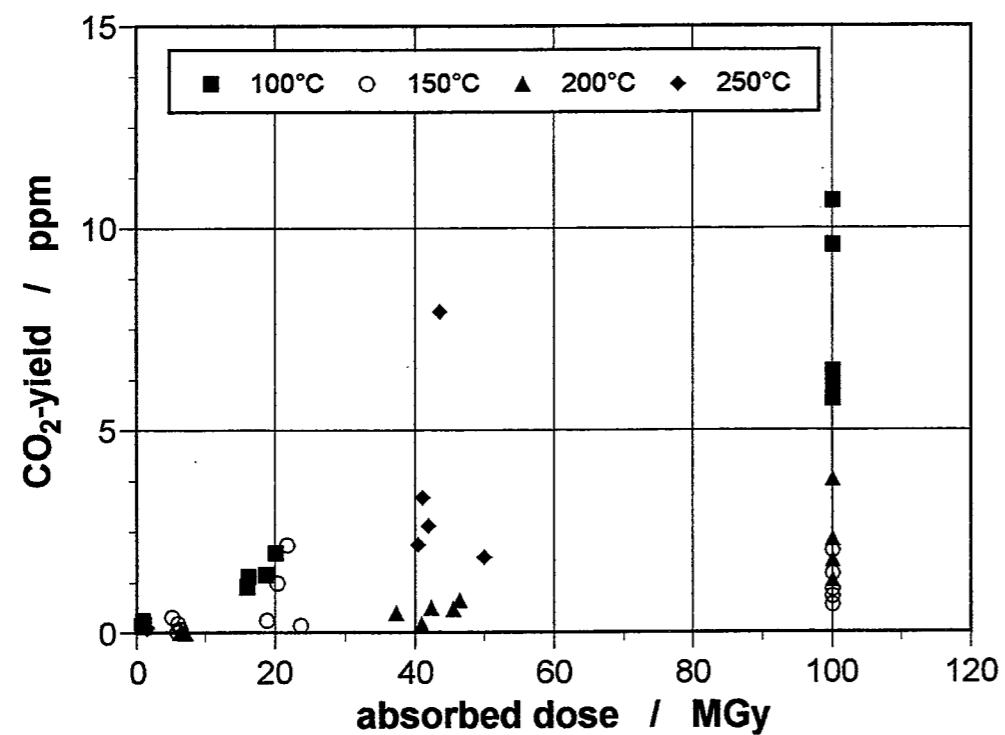


Figure 3: Yield of carbon dioxide vs. absorbed dose at various temperatures for γ -irradiated rock salt in a helium atmosphere.

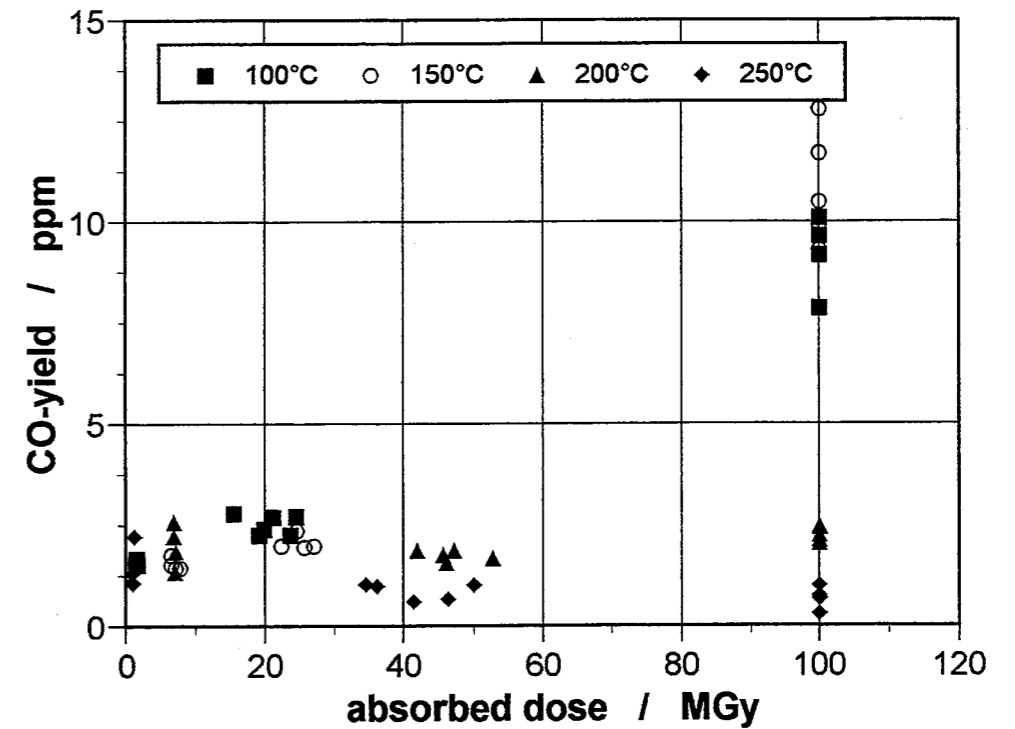


Figure 4: Yield of carbon monoxide vs. absorbed dose at various temperatures for γ -irradiated rock salt in a synthetic air atmosphere.

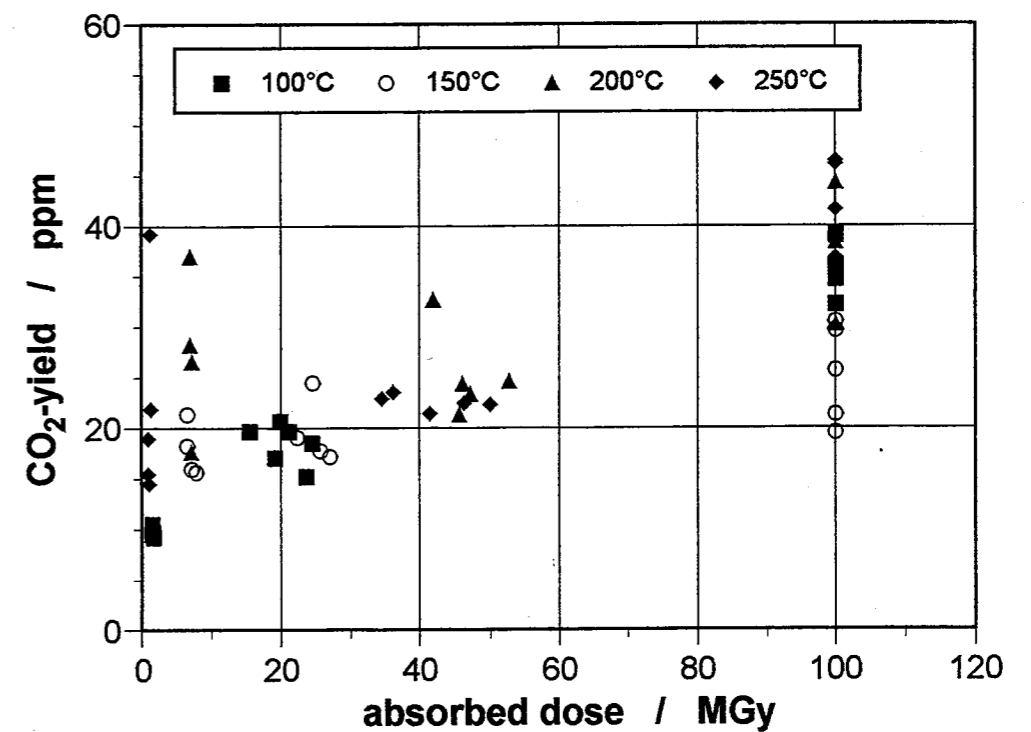


Figure 5: Yield of carbon dioxide vs. absorbed dose at various temperatures for γ -irradiated of rock salt in a synthetic air atmosphere.

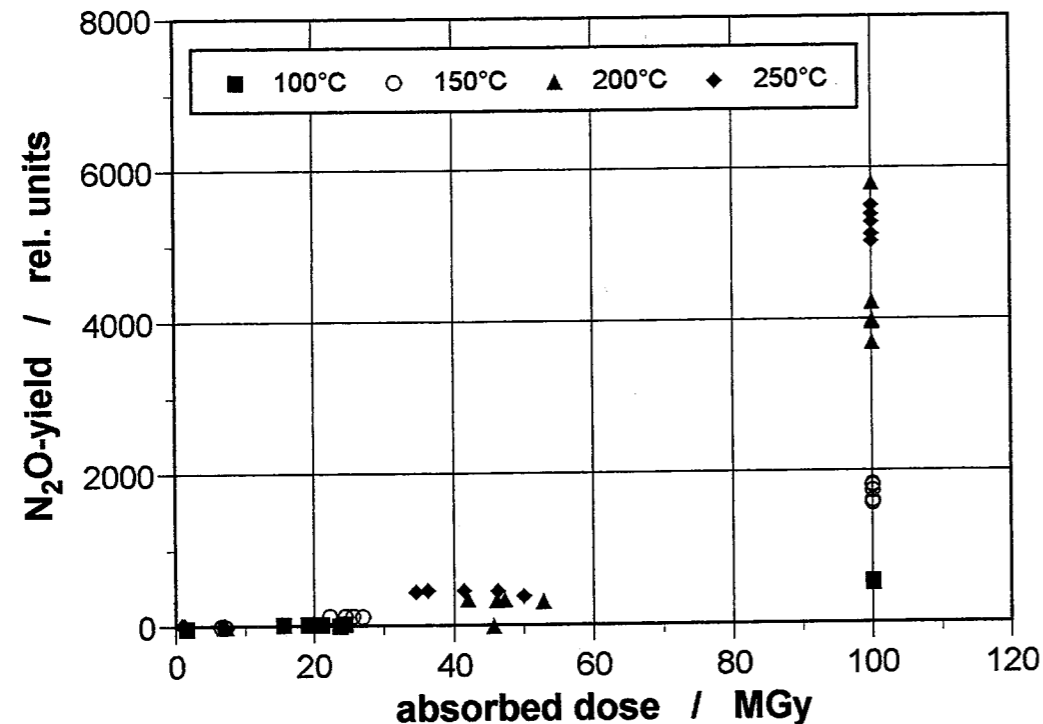


Figure 6: Yield of dinitrogen oxide vs. absorbed dose at various temperatures for γ -irradiated rock salt in a synthetic air atmosphere.

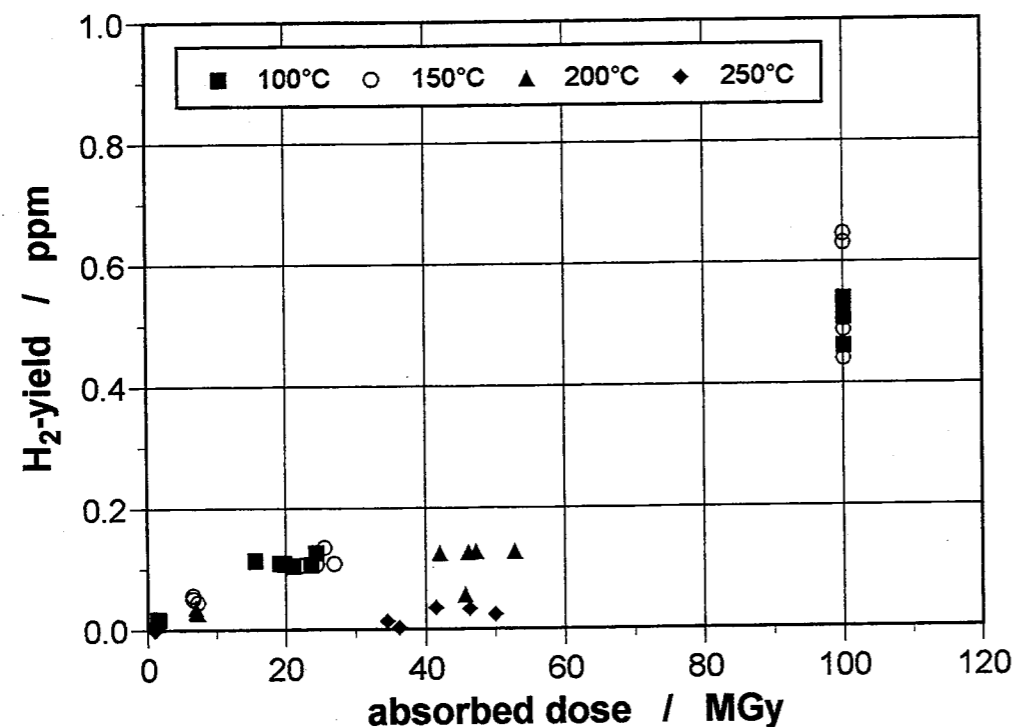


Figure 7: Yield of hydrogen vs. absorbed dose at various temperatures for γ -irradiated rock salt in a synthetic air atmosphere.

3. DISCUSSION

Figures 1 - 3 reveal, that the gas yields depend on radiation dose but only slightly on temperature, when the irradiations are carried out under a helium atmosphere. The generation of hydrogen increases almost linearly with increasing dose, while the CH_4 - and CO_2 -yield seem to level off at the highest doses. The hydrogen is produced by radiolytic decomposition of water. This process occurs either homogeneously in the gas phase or heterogeneously on the salt surface.

In the presence of oxygen, the hydrogen yield is considerably reduced (Fig. 7). This applies generally to all temperatures and radiation doses. In contrast to irradiations in helium, the hydrogen yields in an oxygen atmosphere show a marked dependence on temperature. Hardly any hydrogen is found at 200 °C and 250 °C. As outlined above, hydrogen is formed by two processes. In the homogeneous gas phase reaction hydrogen is produced via the bimolecular reaction of two hydrogen atoms, that are produced by radiolytic decomposition of water molecules in the gas phase.



In the presence of oxygen, the hydrogen atoms react exclusively with oxygen (reaction [3]), as the steady state concentration of hydrogen atoms in the gas phase is orders of magnitude lower than that of O_2 . The resulting $\text{HO}_2\cdot$ radical reacts further, but does not produce H_2 .



The data shown in Figs. 1 and 7 suggest that also a heterogeneous reaction forming hydrogen occurs at the rock salt. In this reaction, water molecule adsorbed at the surface are radiolytically decomposed similar to reaction [1]. However, since this reaction occurs on the salt surface the resulting H atoms are believed to be stabilized on the solid, thus allowing the combination of two such hydrogen atoms (as in reaction [2]). Owing to the dipolar character of the crystal surface, always more water molecules than oxygen molecules should be adsorbed. It follows, that on the salt surface reaction [3] can not effectively compete with reaction [2]. The H_2 -yield in the presence of oxygen, therefore, can be attributed to the

combination reaction of two hydrogen atoms on the surface of the salt crystal. At the higher temperatures low H₂-yields are observed since under these conditions hardly any water is adsorbed at the crystal surface.

Carbon dioxide were found both when irradiations were performed under helium and under air. In a helium atmosphere carbon dioxide is not produced by radiolytic processes. Its appearance in the gas phase is attributed to desorption from the rock salt surface. The same applies to methane. However, both yields are fairly low and exhibit some scatter. In control experiments in which ampoules were exposed to various temperatures but not irradiated, both carbon dioxide and methane were also detected (data not shown). The data in Figs. 2 and 3 suggest an upper yield of about 7 ppm CO₂ and of 0.3 ppm CH₄ per gram salt, respectively.

Desorption from the salt surface depends surely on time. It is expected that desorption will also depend on temperature. Therefore, desorption of CH₄ and CO₂ should occur considerably faster at the higher temperatures and the upper yields should be reached in shorter times, i.e. at lower doses. However, such a dependence is not apparent in Figs. 2 and 3. Quite in contrast, the highest CO₂-yield is obtained at the lowest temperature. It is possible that the release of the gases is facilitated by radiation damage of the crystal lattice. This kind of synergistic effect has been observed previously [Jockwer and Mönig, 1989]. Since the extent of radiation damage is much higher at 100°C than at 200°C, it could outweigh the temperature effect on desorption.

In the presence of oxygen during the irradiation, methane and other hydrocarbons are radiolytically oxidized forming CO and CO₂. Thus, no methane is found in these systems and the CO₂-yield is about fivefold higher than in oxygen-free systems. Some carbon dioxide could also originate from thermal oxidation of hydrocarbons. The data indicate a small temperature dependence for the formation of CO and CO₂. The higher the temperature, the lower the CO-yield while the respective CO₂-yield increases.

N₂O is formed from nitrogen and oxygen via gas phase reactions. The yield clearly increases with temperature. Interestingly, such a strong variation with temperature was not observed by Akram et al. [Akram et al., 1992]. The reaction scheme for the gas phase radiolysis of moist air is very complex [Reed and Konynenburg, 1988]. A variety of products are formed, other products besides N₂O include nitrous oxide, nitric acid and so on. These products have not been determined in the frame of our investigation. The relative yields of the various products depend very strongly on the boundary conditions of the experiment.

From our data, one can estimate the order of magnitude for the radiation-induced gas production that would occur in a repository with disposal of vitrified high level waste in boreholes. Approximately 25 cm of salt around the borehole are affected by radiation. Assuming a borehole diameter of 60 cm, one can estimate the following numbers for the gas production per meter borehole at 10⁸ Gy.

Table 1: *Estimated gas production in an emplacement borehole for vitrified high-level waste at 10⁸ Gy (assuming a borehole diameter of 60 cm and a zone of 25 cm rock salt around the borehole that is affected by radiation)*

gas component	gas production (in l) per meter borehole at 10 ⁸ Gy
H ₂ (in oxygen-free environment)	60.0 l/m
CH ₄ (in oxygen-free environment)	0.7 l/m
CO ₂ (in air)	30.0 l/m

A borehole with a diameter of 0.60 m has a volume of about 280 l per meter length. At 10⁸ Gy the gas production both in the presence of air and in its absence totals less than 100 l. Therefore, only a small pressure increase due to the radiation-induced gas formation should occur. The contribution of this process to the total source term is apparently very low. In aerated systems nitrogen and oxygen are converted into N₂O, but this process also does not lead to a pressure increase. The gas production via other processes such as the formation of hydrogen via corrosion and the pressure increase due the creeping of the salt are much more important for the safety considerations.

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ANALYSES OF RADIOLYTIC GASES RESULTING FROM GAMMA IRRADIATION OF ASSE ROCKSALT PERFORMED AT SACLAY.

M.T. Gaudez, N. Akram, P. Toulhoat, N. Toulhoat, J.M. Palut

ABSTRACT

The radiolytic generation of gases is an issue which has been considered when studying the safety of radioactive waste repositories in rocksalt. During these 5 years of research over 350 samples of ground salt have been irradiated and analyzed in order to elucidate which are the mechanisms in the radiolytic generation of gases in salt.

We have studied the effect of dose and dose rate at different temperature in the amount and nature of generated gases. The irradiated samples were of different composition and granulometry, in this way different backfill characteristics could be simulated. The samples were encapsulated in glass vials prior to irradiation. The gases contained in the vials were analyzed after irradiation. Samples from the same batch were encapsulated in vials inside which different atmospheres were created. In this way the relationship between original oxidizing, reducing, or inert atmosphere, and the obtained gases could be studied.

The way in which the experiments were performed and the obtained results are here described.

1. INTRODUCTION

ANDRA, the French National Radioactive Waste Management Agency, joined the HAW project in 1988 in the framework of European Community agreements FI1W 0199 and F12W 0002. Andra's involvement relates to calculations, laboratory testing and *in situ* measurements. The objective of laboratory work summarized in this report was parametric study, in a laboratory,