GEOCHEMISTRY OF THE HAW TEST FIELD AND OCCURRENCE OF PRIMARY AND SECONDARY GASES

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ABSTRACT

The mineralogical and geochemical situation encountered in the HAW test field is described in some detail. It was found to be slightly different for the two test galleries. About 50 boreholes were drilled in the test field and sealed by packers in order to study the gas release from them and the gas formation in rock salt, which is caused by the presence of heat sources and radioactive sources. In addition, a laboratory program was started for a quantitative assessmment of the various parameters contributing to the gas formation.

MINERALOGY AND GEOCHEMISTRY OF THE TEST FIELD

The Asse salt anticline, situated in the southern marginal region of the North German salt basin, is stratigraphically comparable to that of Gorleben, which is located approximately 110 km to the north.

The two major rock salt horizons, which are envisaged for radioactive waste disposal (i.e., Na2 and Na3), are present at the Asse, and are separated by the carnallitic Stassfurt potash seam (1). They are similarly developed at both sites, showing a particularly more sulfatic upper part of the Stassfurt halite (Na2) immediately beneath the seam. This transitional horizon reaches up to 30 - 50 m in thickness and is also present at the 800 m level of the Asse Salt Mine. The mean compositions of the Na2 at the Asse and at the Gorleben site are shown in Table I, respectively.

TABLE I

Mineralogical Composition of Candidate Disposal Horizons in Permian Rocksalt (wt. %)

	UPPER STASSFURT HALITE	STASSFURT AND LEINE HALITE
MINERAL	ASSE[1]	GORLEBEN[2]
Halite	94.3	96
Anhydrite	4.9	3
Polyhalite	1.5	
Kieserite, Carnallite (?)		
Quarz, Magnesite, Clays	0.13	

[1] approx. 250m profile, [2] according to PTB

The region in which the HAW test field, consisting of two parallel galleries, was opened is unexpectedly different from most of the other parts of the Asse anticline, exhibiting a predominantly horizontal anticlinal structure of the salt layers. Beyond that, there is evidence that the lower boundary of the sulfatic transition zone intersects the emplacement boreholes of the HAW test field. Whereas the major part of the ≥ 500 m thick Na2 consists of halite and anhydrite (Na2βa), the upper portion is enriched in polyhalite and kieserite (Na2βp), resulting also in a higher water content (Fig. 1). For the test field boreholes, this results in water contents of between 0.1 - 0.2 wt.-% in the upper part and of roughly 0.04 - 0.12 wt.-% in the bottom part, which will be heated and irradiated by the heat and radiation sources. These water contents closely correlate with corresponding quantities of hydrated sulfates, as was shown by X-ray diffraction analysis (Table II). This means that also in this case, polyhalite is the main source of water in the rock salt.

Besides the major ions Na^+, Ca^+, K^+, Mg^+, SO^{2-}_4, Cl^-, the following trace elements were analyzed in some detail: Br, Sr, Ni, Fe, Z (1 ppm ≤ c ≤ 40 ppm), and Li, B, Mn, Cu, I, Ba (1 ppm). A special survey was performed for the disposal borehole A2. It was observed, that some elements, e.g. Sr, Li and B, are particularly bound to sulfatic minerals, whereas Br is the only element which showed a strong correlation with halite. All other elements are evenly distributed between sulfatic minerals and halite. Chemical analyses are still under way for a final, fully quantitative survey of the test field.

The presence of the horizontal structure mentioned above creates, together with a slightly inclined bedding, a somewhat different mineralogical situation for each of the two disposal test fields. Particularly in gallery B, this situation causes differences between the various emplacement boreholes, thus complicating the in situ situation.

IN SITU GAS FORMATION

In the final repository, it is planned to drill 300 to 600 m deep boreholes from the 800 m level to emplace the canisters containing the vitrified high-level radioactive waste. These canisters will have a heat generation of 1.8 kW/m, a gamma dose rate of about 10^3 Gy/h and a neutron flux of about $2 \cdot 10^9$ n/m x• s.

Due to the emplaced waste, the rock salt in the surroundings of the borehole will be heated up to 200 °C and irradiated with a dose of about 10^8 Gy within the first 100 years. For an assessment of the long-term safety of a repository, it is of paramount importance to investigate all parameters which could conceivably influence the gas generation and the gas liberation, respectively. Several

TABLE II

Sulfate Contents of the HAW Test Field Rock Salt
(values given below plus the halite matrix = 100 wt. -%)

ROOM A

			Emplacement Boreholes		
Depth (m)		A1	A2	A3	A4
0 - 8	Anhydrite	0.65	2.20	1.24	2.03
	Polyhalite 1.45	1.30	1.75	2.54	
8 - 15	Anhydrite	1.60	3.65	1.17	3.50
	Polyhalite	0.45	0.42	0.34	0.40

ROOM B

			Emplacement Boreholes		
Depth (m)		B1	B2	B3	B4
0 - 8	(still to be analyzed!)				
815	Anhydrite	1.45	1.31	2.38	1.99
*	Polyhalite 2.41	1.50	1.62	0.71	

pathways can account for the release and the formation of gases. They comprise:

- The thermally-induced liberation of gases from the salt adsorbed to crystal boundaries or trapped in small inclusions,
- mineral modifications and alterations due to heating,
- and radiation-chemical reactions.

The latter pathway includes the gas-phase radical reaction induced by gamma-radiation of the borehole atmosphere, gamma-radiolysis of solid rock salt, and reactions of solid, chemically unstable, radiolytic products, e.g. colloidal sodium.

In order to obtain information on these effects and the liberated volatile components, an in situ and laboratory investigation program was set up within the HAW project. In view of their potential danger, the most important gases are the flammable gases hydrogen and methane, and the corrosive gases H_2S, SO_2, NO_x, Cl_2, and HCl in combination with H_2O. All of these gases have been detected previously in in situ tests or in laboratory experiments. However, a coherent picture of their formation in a repository in rock salt has as yet not emerged.

In the test field, about 50 special boreholes were drilled at different distances between 0.73 m and 6.50 m from the center of the emplacement boreholes (6 to 7 at each test site). These boreholes with a depth of 15 m and a diameter of 76 mm have been sealed with mechanical packers. A principal drawing of such a packer is shown in Fig. 2. It consists of two independent viton seals which are spanned and pressed against the borehole surface by a nut at the top. All surfaces of the packer and the valves which may have contact with the gas in the borehole are coated with teflon in order to avoid adsorption or chemical reactions (e.g. corrosion). The packers have a length of 4 m in order to seal the borehole outside the zone of microfissions generated by excavation of the gallery. Three teflon tubes for gas sampling pass through the packers ending in different depths in the borehole in order to determine gas sedimentation in addition to the qualitative and quantitative analyses. These tubes are closed with gas-tight valves at the top. Via these valves, gas samples are taken out of the boreholes. At the top, the borehole is enlarged to take up the gas valves. The enlargement is covered by a lid on the gallery floor to protect the packers from the traffic in the test field.

After installation of the packers, the boreholes were evacuated and filled with pure nitrogen. They were pressurized to 1.5 bar to avoid migration of gas components from the ventilation air of the mine into the borehole, to indicate the tightness of the borehole, and to take gas samples more easily. Additionally, gas samples are also taken out of the gap between the steel liner and the salt of each emplacement borehole.

The gas analyses are performed in an underground laboratory within the test field which is equipped with a gas chromatograph and an ion chromatograph. In order to take the gas samples and transport them to the laboratory for analysis, gas sampling bags or gas sampling bulbs made of glass are used.

This gas analysis program was already started prior to switching on the electrical heaters on November 8, 1988 and about two years before the emplacement of the radioactive sources. Since gas sampling takes place at different distances from the emplacement borehole, it will be possible to determine:

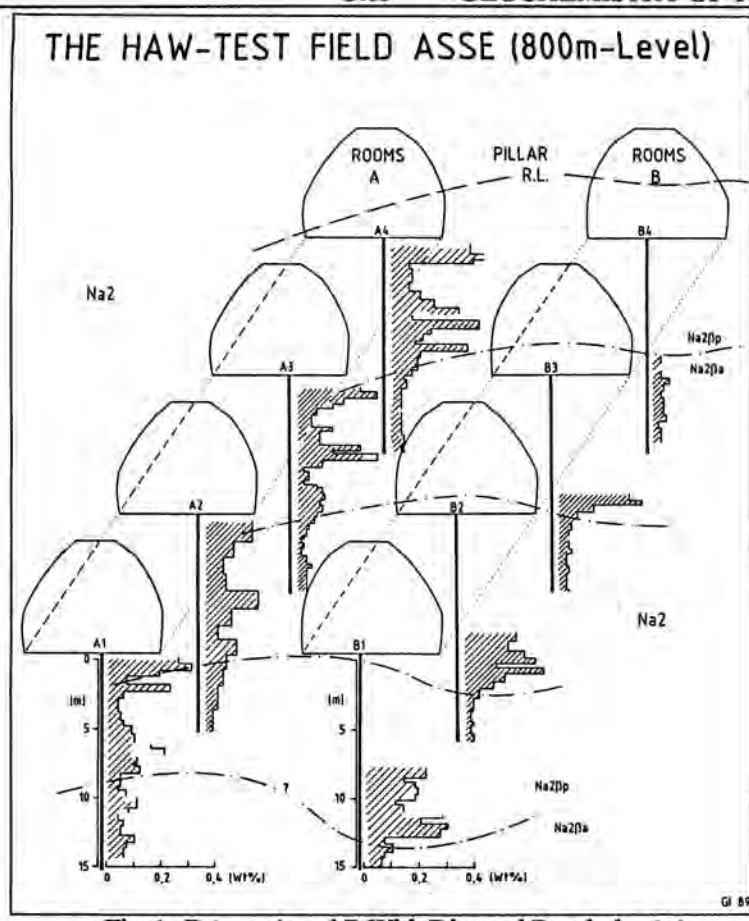

Fig. 1. Rooms A and B With Disposal Boreholes 1-4.
Water Contents of the Rocksalt. (R.L. = Reference Layer).

The liberation of gases already present in the rock salt at ambient temperature,

- the generation and liberation of gases as a result of elevated temperature and,
- the generation and liberation of gases as a result of elevated temperature and gamma-radiation.

In the sealed boreholes within the HAW test field, we found the following components with their concentrations liberated at ambient temperature:

CO_2	up to 600 vpm (= 600 ml/m^3)
CH_4	up to 120 vpm
C_2H_6	up to 23 vpm
H_2S	up to 40 vpm
H_2O	up to 30 g/m^3

(= 70 % relative humidity at 36°C)

HCl was not detected at ambient temperature in the test field.

For comparison, the maximal concentrations which were detected in boreholes in the Asse salt mine (2), are:

H_2S	up to 6,000 vpm (0.6 Vol.-%)
HCl	up to 280 vpm
SO_2	up to 25 vpm

On November 8, 1988, the electrical heaters were switched on in order to verify the stability of the emplacement borehole liners. Since then, the gas liberation from the rock salt as a function of elevated temperatures up to 250° C was determined. Within the first three months of observation (until the end of January 1989), the concentration of the components hydrogen, methane, carbon dioxide and carbon monoxide increased at both test sites. As an example, the increase of these components in the annulus between the borehole liner and the rock salt is shown:

H_2S	increasing from 0 to 170 vpm
CH_4	increasing from 0 to 160 vpm
CO_2	increasing from 380 to 5,000 vpm
CO	increasing from 0 to 100 vpm

HCl and H_2S have only been found in traces.

For quality assurance purposes, analyses are also performed in the laboratory outside the mine in Braunschweig by mass spectrometry. Additionally, samples are also

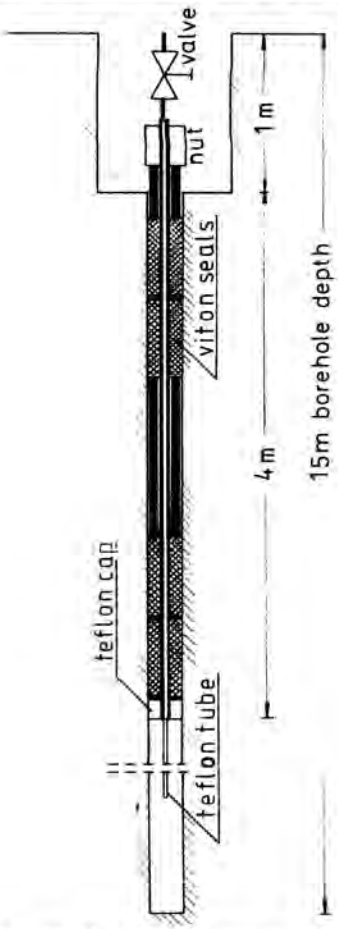

Fig. 2. Principal Drawing of a Mechanically Expanded Packer.

regularly analyzed by other laboratories.

LABORATORY EXPERIMENTS

The in situ experiments in closed boreholes provide only a measure for the equilibrium situation, i.e. a relative measure. In order to determine quantitatively how much gas results from the various processes described above, laboratory experiments are carried out employing salt samples of known mass.

In a first set of experiments, salt blocks of 5 kg, which were freshly cut from the HAW test field, were stored in containers under a nitrogen atmosphere. In order to determine the natural gas desorption, the container's atmosphere was regularly analyzed using gas chromatography. The gas desorption at room temperature is finished now and a typical release curve is shown in Fig. 3. Only CO_2, H_2, CH_4 and higher homologues were desorbed at room temperature. The gas yields were always low, but vary from sample to sample indicating that the mineralogical content has some influence. The highest yield observed was 2 mg CO_2 per kg rock salt with all other gases being at least one order of magnitude lower. These experiments will now be repeated at elevated temperatures up to 200 °C.

Gamma-radiolysis of salt leads to an additional formation of gases. In a first experimental program, salt samples

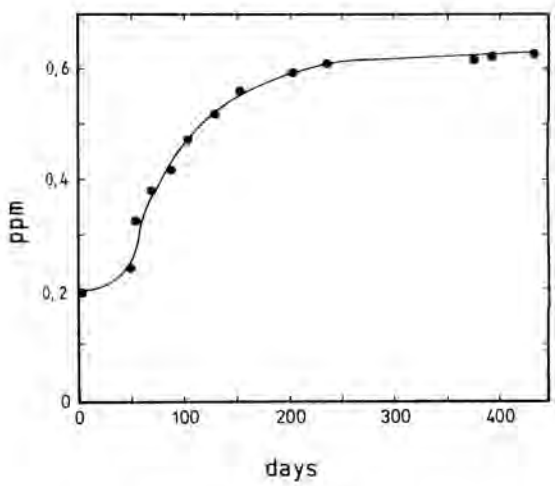

Fig. 3. CO_2 Release From 5kg Rock Salt Blocks at Room Temperature.

were irradiated under air and the total dose, the dose rate, and the temperature during the irradiation were varied. Details on this study are published elsewhere (3).

Increasing dose leads, in general, to increasing gas yields, whereas the dose rate does not seem to affect the results. CO_2, CO, N_2O, traces of CH_4 and at doses > 10 Gy HCl, SO_2 and NO_x were detected. H_2 was notably absent in all samples. Irradiation at 200°C leads to high yields of CO_2 (100 mg CO_2 per kg salt), but CO is radiolytically destroyed. An extensive experimental program has now been initiated in collaboration with the French Centre a l'Energy Atomique (CEA-ANDRA), France.

For a complete understanding of the complex release mechanisms in a repository, information is necessary in addition to the above-mentioned laboratory experiments. Hence, it is envisaged to carry out the following studies:

- Evaluation of colloidal sodium generated by gamma-irradiation and determination of the molecular chlorine yields,
- Evaluation of the influence of containment material on gas-generation,
- Development of a theoretical description of radiation effects in salt,
- Evaluation of neutron irradiation effects in salt,
- Determination of the porosity and permeability of the salt.

CONCLUSIONS

The test fields, which were opened for the HAW disposal test, are now mineralogically and geochemically characterized. Unexpectedly, the salt of the emplacement region at the bottom parts of the boreholes contains a smaller percentage of polyhalite, and thus of water, than was originally anticipated. This is due to a horizontal

anticlinal structure of the salt layers and the presence of the sulfatic transition zone within that region. A somewhat different mineralogical situation is encountered at each of the two test galleries, because of a slightly inclined bedding of salt.

The test field is equipped with about 50 tightly-sealed boreholes for gas collection, and measurements are now carried out for about one year. The purpose of these measurements is the determination of natural gas release, of thermally-induced gas release, and of gas-formation by heat and gamma-irradiation. The interpretation of the in situ measurements will be supported by an extensive laboratory program which comprises the quantitative determination of gas release rates, the study of radiolytic gas formation and liberation, and the investigation of radiation-induced processes in rock salt.

The objective of this investigation is to obtain basic data for the development of a long-term safety concept for a repository of high-level radioactive waste.

ACKNOWLEDGEMENT

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REFERENCES

1. Muller-Schmitz, S., "Mineralogisch-petrographische und geochemische Untersuchungen an Salzgesteinen der StaBfurt-, Leine- und Aller-Serie im Salzstock Gorleben (Niedersachsen, Bundesrepublik Deutschland)," Dissertation Heidelberg, 1985.
2. Jockwer, N., "Influence of Elevated Temperature and Ionizing Radiation on Rock Salt," Proc. of the Joint USA/FRG Workshop on "Salt Near Field Geochemistry," Sept. 22-24, 1987, Albuquerque, N.M., U.S.A.
3. Jockwer, N. and J. Monig, "Laboratory Investigation into the Radiolytic Gas Generation from Rock Salt. A Study Related to the Disposal of High-Level Radioactive Waste," Scientific Basis for Nuclear Waste Management XII, Materials Research Society, Berlin, 1988, in the press.